MARIUS URBONAVIČIUS

HYDROGEN SYNTHESIS USING REACTION BETWEEN PLASMA ACTIVATED ALIUMINIUM AND WATER

SUMMARY OF DOCTORAL DISSERTATION

TECHNOLOGICAL SCIENCES, ENERGETICS AND POWER ENGINEERING (06T)

Kaunas
2018

KAUNAS UNIVERSITY OF TECHNOLOGY
LITHUANIAN ENERGY INSTITUTE

MARIUS URBONAVIČIUS

HYDROGEN SYNTHESIS USING REACTION BETWEEN PLASMA ACTIVATED ALIUMINIUM AND WATER

Summary of Doctoral Dissertation
Technological Sciences, Energetics and Power Engineering (06T)

2018, Kaunas

Doctoral dissertation was prepared in 2013-2017 at Lithuanian Energy Institute Center for Hydrogen Energy Technologies.

Scientific supervisor:

Dr. Darius MILČIUS (Lithuanian Energy Institute, Technological Sciences, Energetics and Power Engineering – 06T).

Editor: Jūratė Kulčickytė-Gutaitė

Dissertation Defence Board of Energetics and Power Engineering Science Field:

Prof. Dr. Habil. Eugenijus UŠPURAS (Lithuanian Energy Institute, Technological Sciences, Energetics and Power Engineering – 06T) – **chairman**;

Prof. Dr. Habil. Artūrs MEDVIDS (Riga Technical University, Physical Sciences, Physics – 02P);

Assoc. Prof. Dr. Saulius MICKEVIČIUS (Vytautas Magnus University, Physical Sciences, Physics – 02P);

Prof. Dr. Habil. Gintautas MILIAUSKAS (Kaunas University of Technology, Technological Sciences, Energetics and Power Engineering – 06T);

Dr. Raimondas PABARČIUS (Lithuanian Energy Institute, Technological Sciences, Energetics and Power Engineering – 06T).

The official defence of the dissertation will be held at 12 a.m. on 13 March, 2018 at the public meeting of Dissertation Defence Board of Energetics and Power Engineering Science Field in Meeting Hall at Lithuanian Energy Institute.

Address: Breslaujos st. 3-202, 44403 Kaunas, Lithuania.
Tel. no. (+370) 37 300 042; fax. (+370) 37 324 144; e-mail: doktorantura@ktu.lt

Summary of doctoral dissertation was sent on 13 February, 2018.
The doctoral dissertation is available on the internet http://ktu.edu and at the library of Kaunas University of Technology (K. Donelaičio st. 20, 44239 Kaunas, Lithuania) and Lithuanian Energy Institute (Breslaujos st. 3, 44403 Kaunas, Lithuania).

KAUNO TECHNOLOGIJOS UNIVERSITETAS
LIETUVOS ENERGETIKOS INSTITUTAS

MARIUS URBONAVIČIUS

VANDENILIO SINTEZĖ PANAUDOJANT PLAZMOJE AKTYVUOTŲ ALIUMINIO MILTELIŲ IR VANDENS REAKCIJAS

Daktaro disertacijos santrauka
Technologijos mokslai, energetika ir termoinžinerija (06T)

2018, Kaunas

Disertacija rengta 2013-2017 metais Lietuvos energetikos instituto Vandenilio energetikos technologijų centre

Mokslinis vadovas:

Dr. Darius MILČIUS (Lietuvos energetikos institutas, technologijos mokslai, energetika ir termoinžinerija – 06T).

Redagavo: Jūratė Kulčickytė-Gutaitė

Energetikos ir termoinžinerijos mokslo krypties daktaro disertacijos gynimo taryba:

Prof. habil. dr. Eugenijus UŠPURAS (Lietuvos energetikos institutas, technologijos mokslai, energetika ir termoinžinerija – 06T) – **chairman**;

Prof. habil. dr. Artūrs MEDVIDS (Rygos technikos universitetas, fiziniai mokslai, fizika – 02P);

Doc. dr. Saulius MICKEVIČIUS (Vytauto Didžiojo universitetas, fiziniai mokslai, fizika – 02P);

Prof. habil. dr. Gintautas MILIAUSKAS (Kauno technologijos universitetas, technologijos mokslai, energetika ir termoinžinerija – 06T);

Dr. Raimondas PABARČIUS (Lietuvos energetikos institutas, technologijos mokslai, energetika ir termoinžinerija – 06T).

Disertacija bus ginama viešame energetikos ir termoinžinerijos mokslo krypties disertacijos gynimo tarybos posėdyje 2018 m. kovo 13 d. 12 val. Lietuvos energetikos instituto posėdžių salėje.

Adresas: Breslaujos g. 3-202, 44403 Kaunas, Lietuva.
Tel. (+370) 37 300 042; faks. (+370) 37 324 144; el. paštas: doktorantura@ktu.lt

Disertacijos santrauka išsiųsta 2018 m. vasario 13 d.
Su disertacija galima susipažinti internetinėje svetainėje (http://ktu.edu), Lietuvos energetikos institute (Breslaujos g. 3, Kaunas Lietuva) ir Kauno technologijos universiteto bibliotekoje (K. Donelaičio g. 20, 44239 Kaunas).

INTRODUCTION

Relevance of the research

Efforts to reduce greenhouse gas emissions and dependence on limited fossil fuel resources lead to development of new cleaner alternative energy sources. Recently, hydrogen fuel cells are considered as promising systems for energy supply, capable of contributing to progress of sustainable energy sources and reduction of total amount of emitted CO_2. Hydrogen is recognized as one of the best energy carriers, when chemical energy is converted into electricity. Therefore, much attention is paid to environmentally friendly and economical methods to extract hydrogen.

Portable electronic devices have become an important inseparable part in human daily life. Functionality of various gadgets demonstrates their fast progress each year. However, current battery technologies are not developed as expected; hence, they cannot ensure required power for longer time of use. Consequently, demand for alternative and effective techniques for energy supply becomes relevant. It is worth mentioning that it is very important for long-life devices in military industry. In this case, proton exchange membrane (PEM) fuel cells can improve operation characteristics, because of larger energy density, fast start and higher efficiency. Moreover, fuel cell will work until hydrogen is supplied.

Hydrogen fuel cells can be used in stationary and portable electronic devices. However, despite the fact that hydrogen has high-energy value and reaction by-products are oxygen together with water, practical application of this technology in low power apparatus is limited due to expensive and complex extraction and storage of hydrogen. Existing external chargers with integrated fuel cells *(Horizon MiniPak ir Inteigent Energy Upp)* confirm relevance of this topic. In addition, Apple Inc. patented the use of hydrogen technologies in smart phones and tablet computers (*US20150249280*) by using expensive metal hydrides for hydrogen storage.

Therefore, previously mentioned hydrogen storage and transportation systems could be replaced by small equipment for hydrogen synthesis on demand (*in situ*), when hydrogen is supplied after its extraction during the reaction between metal and water. Promising *in situ* hydrogen extraction, when reaction between aluminium and water is ensured, can be applied to portable low power devices with PEM fuel cells. On the other hand, water insoluble layer is created on the surface of Al at natural conditions. It stops an access of water molecules on the metal part of Al.

The latest literature analysis reveals a lot of information about different methods used to break or change the structure of barrier layer; and technological solutions for energy generation when Al-water reaction is applied. Nevertheless, activation of Al surface is usually based on expensive or environmentally unfriendly materials and extremely high temperature. However, hydrogen synthesis is very slow and incomplete, i.e. does not fully react. As a result, other unique solutions are needed in order to remove or replace barrier layer at the surface of Al by avoiding expensive alloys and seeking energy consumption as low as possible. Therefore, clean plasma technologies could be applied to an effective change of surface structure.

An object of this research – the new method of Al surface activation in plasma and explanation of processes which affect the mechanism of activation and Al-water reaction.

The aim of the Doctoral Dissertation

The aim of this work is to create technology based on low temperature plasma activation used for surface modification of aluminium powder and to apply modified aluminium powder for hydrogen production during powder reaction with water, which could be used for electricity generation.

Tasks of the Doctoral Dissertation

In order to achieve the objective the following tasks should be solved:

1. Experimentally determine the optimal parameters of activation under gas plasma used for aluminum powder modification (varying the interaction time, gas pressure, discharge power and distance between the plasma source and sample);
2. To investigate the mechanism of Al powder modification and determine how changes of the surface of Al powder depend on variation of plasma activation parameters and interaction time with plasma;
3. Experimentally determine conditions of the reaction between modified Al powder and water ensuring the highest efficiency of hydrogen synthesis (impact of additional materials (NaOH), temperature and amount of water);
4. To evaluate the possibility of the electricity generation, when hydrogen received after Al-water reaction is supplied to the proton exchange membrane fuel cell;
5. To create a γ-Al_2O_3, applied in the catalyst industry, out of the by-product received after Al-water reaction.

Scientific novelty

In the thesis a new method of Al powder surface modification, when low temperature plasma is applied in order to create active Al in water was proposed. Hydrogen generated during the Al reaction with water is suitable for the low temperature proton exchange membrane fuel cells. In addition, method for synthesis of highly pure γ-Al_2O_3, when by-product of activated Al-water reaction is used as a precursor was offered.

Practical value

Results of this work are significant for creation of safe and clean hydrogen generation on demand systems based on the reactions between activated Al and water. This concept could be applied to the fuel cells used in the market for low-power portable electronic devices (external chargers, digital or mobile devices, GPS transmitters or radio equipment used in the military sector, etc.). Practical value of this work also is demonstrated by the possibility to apply this technology for synthesis of marketable aluminum oxide powder used in catalyst production.

Statements carried out for defence

1. Aluminium powder is activated effectively and it remains in such state at least for 6 months after its interaction with low temperature hydrogen gas plasma generated by the magnetron.
2. Plasma treatment leads to transformation of hydrophobic surface of the aluminium powder into hydrophilic, increase of polar molecules concentration and formation of inhomogeneously distributed defects on the surface.
3. Almost 100% of theoretical value of hydrogen amount is generated during the reaction between plasma activated aluminium powder and water, and kinetics of the reaction is mostly determined by water temperature.
4. Hydrogen production during activated Al and water reaction can be applied to the low-power proton exchange membrane fuel cells used for electricity generation on demand.
5. Highly pure nanocrystalline gamma aluminium oxide, with BET surface area > 200 m^2/g, is obtained after by-product of the reaction between activated Al and water is annealed under the atmospheric conditions.

The structure and content of the Doctoral Dissertation

The dissertation is structured as follows: introduction, literature review, methodology, results and discussion, conclusions, the list of references and the list of scientific publications. The dissertation consists of 128 pages including 54 figures, 15 tables and 262 references.

1. LITERATURE REVIEW

This chapter provides an overview of currently existing methods for hydrogen production, the main hydrogen storage techniques and hydrogen generation form the reaction of various metals with water. Literature review presents state-of-the-art methods for the aluminium activation in order to disrupt naturally formed aluminium oxide layer (which acts as barrier for water molecules) and make it water-reactive. Numbers of suggestions have been proposed by other authors for disrupting the protective layer and accelerating hydrogen production, including mechanical treatment (ball milling), use of highly alkaline solution or use of additional metals (Ga, In, Sn and etc.), oxides or inorganic salts additives. However, some techniques are still too complex and others are harmful, expensive or need elevated water temperature for effective reaction with water. Therefore, a novel method for Al surface modification under glow discharge plasma treatment was proposed and studied in this thesis. Plasma is considered as environmentally-friendly process. Also the possibilities of Al-water reaction by-product regeneration and reuse were discussed.

2. EXPERIMENTAL SETUP AND METHODOLOGY

2.1. Experimental investigation

Modification of aluminium powder was carried out in a physical vapour deposition system which is installed at LEI Centre for Hydrogen Energy Technologies. Design of the system is presented in Fig. 2.1 a. Sample holder, magnetron connected to the power source and a shutter between sample and magnetron were located in the vacuum chamber. DC power supply (3 kW, Advanced Energy DC Pinnacle 3000) was coupled with pulse generator (Advanced Energy Sparc-le 20). Frequency of generated pulse was 20 kHz, where duration of positive signal was 5 µs. A two-stage vacuum system including rotary and diffusion pumps enabled and maintained a base pressure of $1.5 \cdot 10^{-3}$ Pa. Circular magnetron with Al target (diameter 10 cm) was used as the source of hydrogen gas plasma. Aluminium target with purity of 99.999 % was obtained from Kurt J. Lesker Company. Whereas hydrogen gas with purity ≥ 99.999 % (5.0 grade) was purchased from AGA Company.

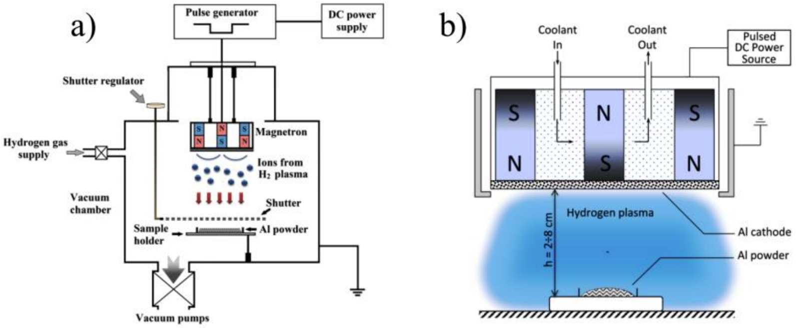

Fig. 2.1. Vacuum system (a) and magnetron (b)

The untreated Al powder was kept in the closed ceramic vessel under ambient conditions. During each experiment, about 0.5 g of aluminium powder was evenly distributed in a stainless steel holder which was placed in vacuum chamber under the magnetron (Fig. 2.1 b).

Each time opening the vacuum chamber leads to magnetron target interaction with air and adsorption of oxides, hydroxides or carbon based compounds on the surface. These undesirable compounds may affect Al modification experiments. Therefore the shutter between the sample and the magnetron was closed and the target surface was being cleaned using argon gas plasma for 5 minutes (bombardment of Ar^+ ions). After target cleaning, vacuum chamber was pumped again and hydrogen gas was injected and maintained operating pressure at 13 Pa. The shutter was opened after plasma ignition and the activation process of Al powder began. During the plasma process magnetron as well as vacuum chamber walls were water-cooled. Isolated K-type thermocouple was used to measure the temperature near the sample. A Langmuir probe was inserted in plasma and used to determine ion current density at 4 and 8 cm distance between the sample and magnetron. When the distance is equal to 8 cm, ion current density is ≈ 0.5 mA/cm^2, while at 4 cm it is ≈ 1.1 mA/cm^2. The higher it is, the larger amount of positive ions reach the Al surface during plasma treatment. According to literature [1], the electron energy is 1–2 eV and density could reach 10^{10}–10^{11} cm^{-3} in such glow discharge plasma.

The main technological parameters of aluminium powder activation are given in Table 2.1.

Table 2.1. Technological parameters of Al powder activation by hydrogen gas plasma

Main parameters	Values
Base pressure, Pa	$1.5 \cdot 10^{-3}$
Working pressure, Pa	13
H_2 flow rate, ml/min	9
Al target diameter, cm	10
Magnetron operating voltage, V	250–260
Magnetron operating current, A	0.3–1
Distance between sample and magnetron, cm	2–8
Ionic current densities, mA/cm^2	≈ 0.5 and 1.1 (at distance of 8 and 4 cm)
Activation time, h	1–20
Temperature during activation, °C	80–180 (depends on the activation parameters)

The unmodified Al powder poured into water floats on the top of the distilled water surface and barely reacts with it. Modified Al powder reacted with distilled water without any additives, however, reaction kinetics were relatively slow. Therefore, a small amount of sodium hydroxide (0.05 M NaOH solution) was used as reaction promoter to slightly increase the concentration of OH groups and enhance the reaction kinetics. Hydrogen generation during the reaction of Al powder and water was investigated using custom made laboratory stand. An inverted burette (Pyrex 250 ml) filled up with water was used to quantify hydrogen production volume, where the quantity of H_2 gas was measured from change of water level in the burette. Burette has graduated scale in steps of 1 ml Hydrogen generation yield was defined by integrating the H_2 flow with time until the H_2 production flow dropped to near zero level. During the reaction, temperature of water was maintained using universal stirred water bath (BWT-U).

Experiments of electric energy generation were investigated using proton exchange membrane fuel cell fuel cell (1.5 W, PEM). Hydrogen supply was ensured via plasma modified Al powder and water reaction. Moisture trap was introduced between reaction tank and energy generation unit in order to prevent fuel cell against contamination. Renewable energy monitor from *Horizon* with constant resistance load of 2 Ω was used to measure generated power. Measurements were performed at different concentration of NaOH (0.025 M, 0.05 M and 0.1 M) and temperature points (25°C and 35°C).

The solid by-product (white sediments) was produced during the reaction between the modified aluminium powder and water. This by-product was used as a precursor for synthesis secondary-use product. The by-product of the reaction was dried under ambient conditions and annealed in two steps at 280 °C and 500 °C for 20 h under atmospheric conditions using a laboratory oven (SNOL 7/1300L), yielding boehmite and pure gamma aluminium oxide, respectively. A heating rate of 3°C/min was used to reach the specified temperature. Samples were removed from the oven after cooling down to room temperature (4-5 hours). The purity of the obtained γ-Al_2O_3 depends only on the purity of the initial aluminium powders, the working gasses used in the activation procedure, and distilled water. High purity product is very suitable for industrial catalytic processes.

2.2. Analysis methods

Crystal structure of aluminium powder was analysed by X - ray diffraction (XRD) method using Bruker D8 diffractometer. The measurements were performed at 2θ angle in the range 20–70° using Cu cathode Kα radiation (λ = 0.15406 nm) in steps of 0.01° and Lynx eye position sensitive detector. Al powder morphology was characterized using a scanning electron microscope (SEM, Hitachi S-3400N). The elemental composition of aluminium powder was analysed via energy dispersive X-ray spectroscopy (EDS, Bruker Quad 5040). For the top surface chemistry analysis plasma-modified aluminium powder was extracted from the vacuum chamber to the atmosphere (interaction time with ambient air was less than 5 min) and transferred to X-ray photoelectron spectroscope (XPS, PHI 5000 Versaprobe) where chemical composition of the surface was measured. The signal observation depth of the XPS method is approximately 5–10 nm. Sorptometer Kelvin 1042 was used to measure Brunauer–Emmett–Teller (BET) surface area of Al powder, reaction by-product and gamma alumina. Concentrations of oxygen and hydrogen within the samples were measured using a gas analyser (HORIBA EMGA-830) based on inert-gas-fusion method. The samples were loaded into the graphite crucibles and heated by the impulse furnace (up to 2000 °C) which nominal power is 8 kW.

3. RESULTS AND DISCUSSION

3.1. Experimental study of other metals exposed to the hydrogen gas plasma

Results of previous experimental studies showed that hydrogenation of metals under low temperature hydrogen gas plasma, according to the methodology presented in this thesis, leads to metal hydride formation after certain time. Generally a formation of metal hydride phase can be described as a multi-step process [2]: firstly, H_2 molecules are physically adsorbed on the metal surface because of the Van der Waals force; secondly, H_2 dissociate into atoms and chemisorption takes place; finally, H atoms diffuse along the grain boundaries into the bulk where nucleation and growth of metal hydride start. Usually, the dissociation of H_2 molecules is ensured by the use of catalysts (e.g. Pd) which also prevents surface oxidation. But in case of plasma treatment, there is no need for the catalyst because plasma consists not only of hydrogen molecules but also of atoms, energetic ions, active radicals, electrons and photons. During the hydrogen plasma interaction with metal, hydrogen ions can penetrate inside the metal surface and create the dynamic surface area with new paths for hydrogen penetration inside the bulk.

Formation of MgH_2 occurs under hydrogen pressure of 30 bar and at temperature of 350–400 ºC [2]. Moreover, the process is quite slow. However, during the hydrogenation process of Mg films using hydrogen gas plasma, according to the methodology was described, MgH_2 peaks were observed after 3 hours of hydrogenation and intensity of peaks even increased after 5 hours of H_2 plasma treatment, $2\theta = 29^\circ$, 35.7° and 39.8° (Fig. 3.1, black balls) [3]. Plasma can bypass the thermodynamic requirements.

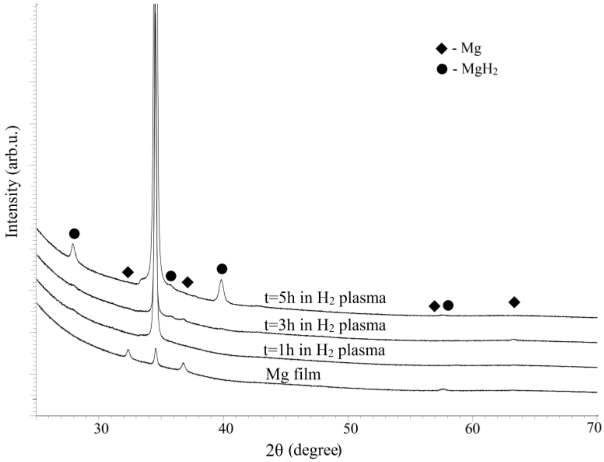

Fig. 3.1. XRD patterns of Mg films before and after hydrogenation in H_2 plasma for t = 1h, 3h and 5h

Plasma treatment can initiate a simultaneous formation of defects, vacancies and dislocations in Mg film which act as new paths for adsorbed hydrogen atoms to penetrate into the bulk of material. Furthermore, plasma removes oxide and hydroxide species formed on the Mg surface, which tends to decrease the hydrogen absorption kinetics.

Solid metal hydride solution, which is called the α-phase, is formed while the hydrogen concentration is relatively low in the bulk (H atoms are randomly distributed in the metal lattice). Usually the XRD technique does not register this phase. When the absorbed hydrogen concentration increases up to the limit value, the α-phase transforms into the crystalline metal hydride phase (XRD peaks registered). The increase of XRD peaks indicates the formation of crystalline structures while shift of peaks shows stresses inside the film.

According to these changes in Mg film after hydrogen plasma treatment, it was assumed that aluminium hydride (AlH_3) could be synthesised and hydrogen could be stored inside the lattice of aluminium in the same way.

3.2. Structural analysis of aluminium powder and determination of O/H gas content before and after plasma activation

The optimal conditions for Al powder activation in plasma were determined experimentally. The activation of Al was considered to be successful when Al powder immediately sank after immersion into the water and started to react by releasing hydrogen gas Unsinkable Al powder indicates high hydrophobicity of the surface and water molecules are repelled without reaching metallic part of Al. In all cases, the working H_2 gas pressure of 100 mTorr (13 Pa) was chosen as the best one and sufficient for plasma activation. Plasma was instable at lower or higher gas pressures. Besides the activation process, it was aimed at obtaining AlH_3 structure which can produce 1.8 times more hydrogen than pure aluminium. Usually formation of AlH_3 requires extremely high pressure of H_2 gas ($\approx$ 10 GPa) but reactive plasma could destroy the oxide barrier and initiate diffusion of H atoms into the bulk of Al.

Aluminium powder was modified under hydrogen gas plasma at 250 W for 1 and 3 hours. A working distance between the sample and magnetron varied from 4 cm to 8 cm. However, the XRD analysis of Al powder did not show any significant structural changes after plasma treatment under altered conditions (Fig. 3.2). XRD patterns include cubic aluminium peaks with crystallographic orientations (111), (200) and (220). Small peak at $2\theta = 41.8°$ can be identified as aluminium oxide (Al_2O_3). X-ray diffraction did not register any structural changes even after longer period of plasma treatment. Kβ radiation and Ni absorption edge are generally achieved because of Nickel attenuation filter equipped in device. Structure refinement of XRD patterns ($R_{wp} \approx 4$) was performed using TOPAS software and crystallite size of Al powder increased from 113 nm up to 125 nm after modification in plasma. Despite the altered plasma activation conditions, peaks intensity and full width at half maximum remained almost unchanged. Whereas, lattice parameter was almost identical $a_{Al} = 4.048$ Å and fluctuated only in the range of ± 0.002 Å. These minor fluctuations could be related to the instrumental error.

Buckley and Birnbaum studied hydrogen introduction into aluminium foil using cathodic plasma charging technique but X-ray diffraction registered near zero change in Al lattice parameter [4]. These results did not correlate with the hydrogenation of other metals with cubic orientation where lattice expansion of $\approx$2,9 Å^3 was exhibited. However, this small change was associated with the formation of hydrogen–vacancy complexes in the near surface layers of Al. As the amount of hydrogen–vacancy complexes increases, their agglomeration into larger ones and formation of hydrogen bubbles can be observed [5]. Later, Xie et al. presented a model which confirmed that intensive flow of hydrogen ions/atoms upon the metal surface can create point defects and vacancies [6].

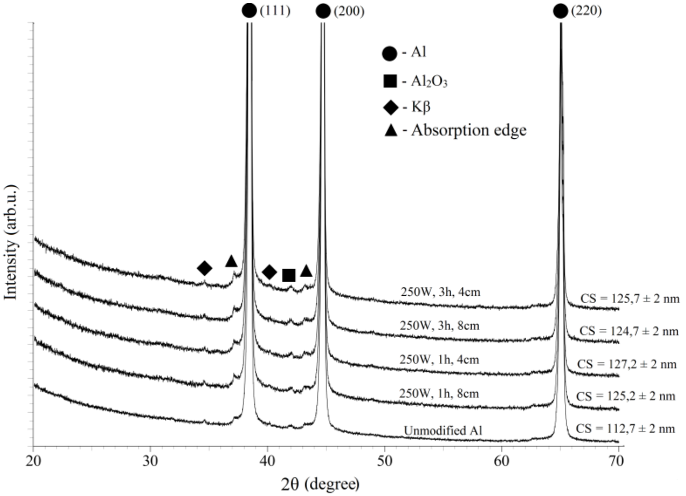

Fig. 3.2. XRD patterns of unmodified Al powder and plasma modified at 250 W and 8 cm for 1 h; at 250 W and 4 cm for 1 h; at 250 W and 8 cm for 3 h; and at 250 W and 4 cm for 3 h

Formation of alane phase (AlH_3) is a challenge because of low decomposition temperature which varies from 60 to 100 ºC depending on structural phase while MgH_2 decomposes at 300 ºC [7,8]. Synthesis of MgH_2 is much more favourable than AlH_3 due to its thermal stability. Additionally, ultra violet light emitted during the plasma process can further accelerate decomposition of alane. It is possible that formation and decomposition of AlH_3 occur simultaneously on the Al surface leading to the change of surface layer during plasma treatment. This layer undergoes the intensive migration of H atoms accompanied by adsorption, desorption, relaxation and defects formation.

In this case, the temperature near sample holder was insignificantly dependent on the changeable distance between the sample and magnetron, and varied from 100 ºC – 8 cm to 112 ºC – 4 cm (Table 3.1). Therefore, too high plasma temperature could be one of the main reasons why AlH_3 was not synthesised. Processes of synthesis and decomposition are very likely to occur simultaneously. In the future, it is recommended to cool down the holder of Al powder at temperatures close to 0 ºC during the hydrogen plasma treatment.

Table 3.1 presents the results of O/H content within unmodified and plasma modified Al powder. Although oxygen concentration of initial and plasma treated Al powder remained almost the same after plasma modification, the content of hydrogen decreased roughly 3 times. Higher hydrogen content of untreated powder indicates that not only native aluminium oxide is formed but aluminium surface is passivated by hydroxides as well. However, gas analyser cannot distinguish which part of hydrogen is adsorbed on the surface and which is introduced into the near surface structure. Therefore the decreased amount of hydrogen could be related to removal of adsorbed OH groups and C–H compounds on the surface because hydrogen is a powerful reducing agent and to the small amount of hydrogen introduced into the Al structure. Buckley and Birnbaum observed that very small amount of hydrogen (up to 1000 ppm) was introduced in the surface layer of Al foil [4]. The main pathways for hydrogen in the surface layer of Al are associated with vacancies created by plasma. This result could be the sign of creation of restructured surface.

Table 3.1. O/H content of unmodified and plasma modified Al powder

Sample	Mass, g	O, wt. %	O error	H, wt. %	H error
Unmodified Al	0.05	2.7176	±0.5 %	0.3142	±2 %
250 W, 3 h, 4 cm, $T_p = 112$ °C	0.05	2.7537	±0.5 %	0.1193	±2 %
250 W, 3 h, 8 cm, $T_p = 100$ °C	0.05	2.4462		0.1068	
250 W, 1 h, 4 cm, $T_p = 112$ °C	0.05	2.7233		0.1201	
250 W, 1 h, 8 cm, $T_p = 100$ °C	0.05	2.6779		0.1179	

However, hydrogen ions are very small and potentially can induce changes and formation of vacancies at the very top surface of the particles or Al/Al_2O_3 interface (down to several atomic monolayers), but if hydrogen plasma modifies only the top surface of aluminium particles without changing the long range lattice structure (bulk material properties) these alterations would be not observable by the XRD technique (information depth of XRD ranges from several micrometres to a few hundred micrometres) therefore use of other analysis techniques is needed.

Under mentioned conditions modified Al powder showed enhanced surface wettability and demonstrated the best reaction with water kinetics and highest hydrogen yield.

3.3. Surface morphology and elemental analysis of unmodified and plasma modified aluminium powder

At first glance, modified and unmodified Al powder did not differ. In both case it was a fine, grey powder. Agglomerations of metal particles were not observed.

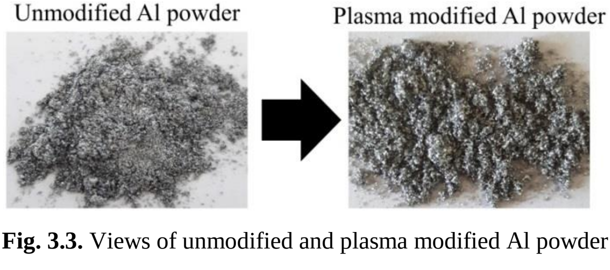

Fig. 3.3. Views of unmodified and plasma modified Al powder

Physical surface bombardment by ions from plasma could additionally enhance the effect of hydrophilicity because of slightly changed surface roughness [9]. Fig. 3.4 presents SEM views of untreated Al powder (a-c) and Al powder modified at 250 W and 8 cm distance for 1 hour (d-f) under hydrogen gas plasma. Presented pictures correspond to different magnifications (scale bar 100 μm, 5 μm ir 3 μm). Al powder modified under previously mentioned conditions (by changing time and distance) demonstrated pretty similar morphology in all cases. Activation at lower distance than 4 cm led to the melting of Al surface. Comparing Al powder before and after plasma modification, the shape of Al particles did not appear to be changed. Irregularly shaped particles were observed in all samples, which size varied from 10 ± 5 μm up to 80 ± 20 μm. Untreated powder surface seems to be relatively smooth (Fig. 3.4., b-c).

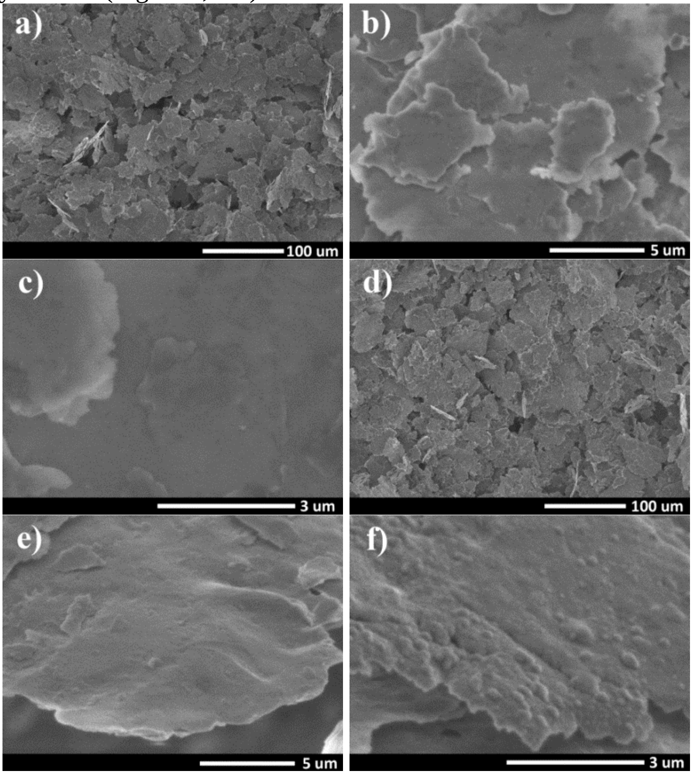

Fig.3.4. SEM images of untreated Al powder (a-c) and H_2 plasma modified at 250 W and 8 cm distance for 1 h (d-f)

Hydrogen can cause defect formation and induce cavitation/blistering effect [10]. However, surface of Al powder has not changed significantly after H_2 plasma treatment. Some areas of modified Al powder revealed irregularities and micro cracks. As well inhomogeneously distributed bubble structures were observed on the surface of Al powder particles after plasma treatment (Fig. 3.4, f). The size of these bumps varies from 100 nm up to 500 nm. It is well known that hydrogen atoms could agglomerate in molecules and form bubbles at the metal-oxide interface during hydrogen ion irradiation [11]. Such bubbles formation mechanism is related to the complexes of hydrogen–vacancies in the surface layer of Al where hydrogen atom can leave the vacancy and diffuse to the metal-oxide interface. Low solubility of hydrogen in aluminium leads to the clustering of hydrogen atoms at the vacancy defects and metal-oxide interface [10]. The excessive amount of hydrogen at the interface leads to the raised internal pressure which pushes the native oxide layer outwards until the visible bubbles are formed [10,12]. Smaller bubbles can be merged into larger ones. On the other hand hydrogen can also dynamically interact with metal side (under the native oxide layer) without formation of visible blisters or morphology change [10]. Therefore SEM does not indicate a lot of characteristic changes in surface morphology, but oxide layer could be drastically weakened.

Though aluminium oxide act as a barrier, it is possible that small part of hydrogen atoms could diffuse into the bulk along the grain boundaries and form solid solution which was not registered by X-ray diffraction. Such effect leads to the higher surface energy and result some irregularities and rupture of the near-surface area. Defects are a pathway for water molecules to reach fresh aluminium metal surface and initiate Al-water reaction.

Surface area (BET) of untreated Al powder was 3.51 m^2/g meanwhile it increased slightly up to 3.75 m^2/g after plasma treatment. This is the result of plasma bombardment with ions and surface restructuring (dynamic alterations in the surface layer). Smaller particles with larger specific surface area produce hydrogen at higher rate. Moreover, hydrogen could generate high stresses which could initiate top surface irregularities and formation of defects.

EDS elemental composition results did not show any significant change in O/Al ratio after plasma modification at 250 W, 8 cm for 1 hour comparing with unmodified Al powder (before plasma – O/Al = 0.030; after plasma – O/Al = 0.031) and this confirms the assumption that plasma treatment changes only the top surface of Al powder. Small content of oxygen can be attributed to the presence of native oxide layer which is formed upon metal exposure to air. Defective oxide layer could be formed under hydrogen ions treatment from plasma.

3.4. Surface chemical analysis of aluminium powder

Effective surface wettability and Al-water reaction strongly depends on the chemical properties of the surface, accumulated charge and functional molecule groups. In contrast to XRD, XPS (X-ray photoelectron spectroscopy) is a surface sensitive technique and can provide more information on the small scale changes at the very top surface of the Al powder particles (up to 10 nm). XPS measurements observed oxygen, carbon and aluminium which are present on the surface of aluminium powder particles before and after hydrogen plasma modification (Fig. 3.5, a). Unmodified Al surface composition consists of 45.3 % of C, 19.5 % of Al and 35.2 % of O (Fig. 3.5, b). The majority of materials exposed to the atmospheric air (gaseous compounds are captured from air) have a naturally formed thin layer of carbon/hydrocarbon, which is called adventitious carbon [13,14]. The thickness of the surface carbon layer is up to 2 nm [15]. O and Al indicate the presence of the aluminium oxide and hydroxide layer which acts as a barrier and prevents aluminium-water reaction. In all cases, after plasma treatment the composition of Al powder surface has changed almost equally (with slight variations of ± 1 % from the mean value). The average values of C, Al and O were determined to be 14.3 %, 31.2 % and 54.5 %, respectively. The amount of the surface carbon C1s decreased by more than 3 times (from 45.3 at. % down to 14.3 at.%) after plasma modification. Such significant reduction of carbon content could be related to the physical and chemical carbon desorption initiated by plasma.

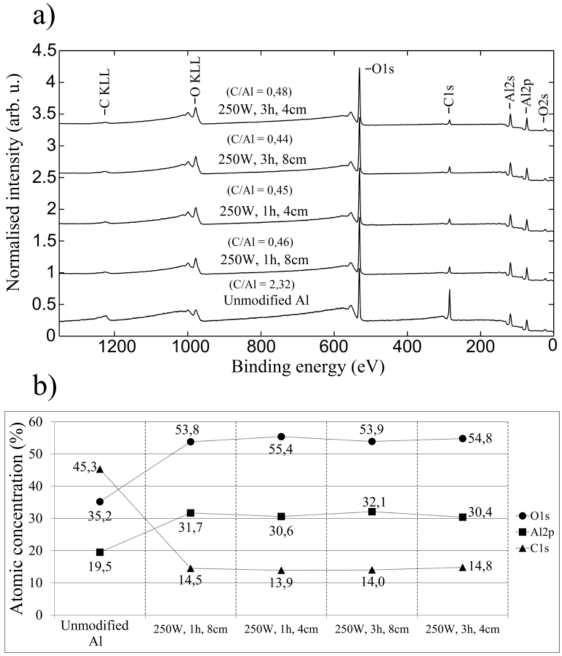

Fig. 3.5. XPS survey scan of aluminium powder surface before and after hydrogen plasma (a) and atomic concentrations of unmodified Al powder and plasma modified at 250 W and 8 cm for 1 h; at 250 W and 4 cm for 1 h; at 250 W and 8 cm for 3 h; and at 250 W and 4 cm for 3 h

Presumably, a part of the surface carbon was sputtered by ions arriving from the hydrogen gas plasma or desorbed as hydrocarbon molecules (volatile C_xH_y compounds). Also it is known that changes of surface chemistry can be induced by ion bombardment and by accidental mixing of excited surface atoms (which bonds with other atoms are weakened) [16]. In the ideal case, after modification in plasma the concentration of surface carbon should be near zero. However, small amount of carbon was readsorbed on the active sites of Al powder produced by plasma treatment. The most probable source of the observed carbon was the adventitious carbon from ambient air to which plasma-modified Al powder was exposed during transfer from vacuum chamber to the XPS equipment (in less than 5 min). The deposits from the residual gases inside the plasma treatment or XPS chambers are less likely due to the short take away time (roughly 1 min) from the plasma treatment chamber and high vacuum (10^{-7} Pa) inside the XPS.

Modified Al powder became hydrophilic and sank instantly after immersion in water. Hydrophilicity is related to the formation of polar molecules/groups which increase surface tension and are capable to form hydrogen bonds [17]. Thus transformation from the stable $Al_2O_3/Al(OH)_3$ layer to the modified $Al_2O_3/Al(OH)_3$ layer could change the initially hydrophobic Al powder to the hydrophilic by increasing quantity of the unsaturated bonds on the very top surface.

Carbon plays an important role in the exchange of surface chemical state and wettability. Ratio of carbon and aluminium atomic content C/Al could be used as a relative evaluation of the surface activity [17]. Hydrophobic surface always has relatively large C/Al ratio [17]. A higher C/Al ratio indicates that the surface has adsorbed a lot of long-chain carbon based molecules. Plasma treatment can terminate these chains leading to the decrease of C/Al ratio. In our case, the C/Al ratio was 2.32 for initial Al powder and 0.44–0.48 after plasma modification (Fig. 3.5, a).

Basically carbon chains are linked together, thereby forming a non-polar C-C bond, which increases hydrophobicity of the surface [17]. Reduced number of non-polar groups and increased surface energy leads to the formation of strongly polar functional groups (carbonyl or carboxyl) on the surface. Surface polarity is an important feature, which determines wettability [18]. Hydrophobicity is related with unique electronic structure, which prevents hydrogen bonding with interfacial water molecules, while polar molecules (groups) increase the hydrophilicity of the surface because of the number of unsaturated polar sites [18].

Indeed, in the conducted experiments it was observed that after plasma treatment C1s peak broadened on the higher binding energy side, which indicates not only the decrease of non-polar carbon C–C bonds but also the formation of polar groups (responsible for the hydrophilicity) at the surface.

In order to better understand plasma modification mechanism of Al powder, XPS fitting analysis of C1s and Os1 peaks was performed.

Fig. 3.6 shows deconvolution of surface carbon C1s peak of untreated (a) and plasma treated (b) aluminium powder. C1s peak was observed to consist of four components: non-polar C–C bonds (285.0 eV); the rest are polar groups [17], carbon with single bonded oxygen C–O (286.2 eV), carbon with double bonded oxygen C=O (288.0 eV) and carboxyl groups COO$^-$ (289.2 eV).

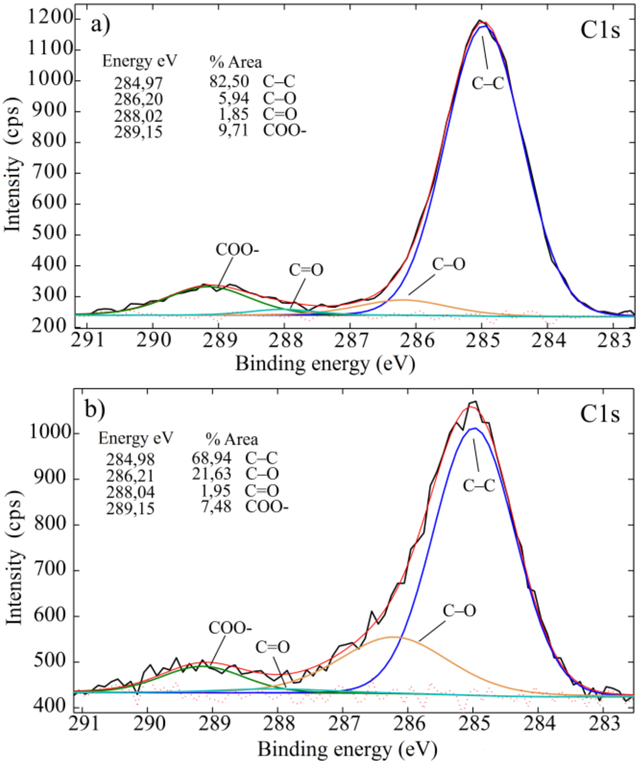

Fig. 3.6. C1s peak fitting of unmodified (a) and plasma modified (b) Al powder at 250 W, 8 cm for 1 h

Fig. 3.6 a shows that in case of unmodified Al powder non-polar C–C bonds account for 82.5 % of the total peak area whereas cumulative peak area of the remaining polar groups accounts only for the 17.50 %, giving the approximate ratio of polar and non-polar groups equal to 0.21.

Plasma treatment led to the formation of the more oxidized carbonaceous species on the surface of plasma-modified aluminium powder. Significant decrease of the amount of non-polar (C-C) groups to 68.9 % and increase of polar groups (C–O, C=O and COO$^-$) up to 31.1 %, which are responsible for hydrophilicity of the surface was registered after plasma modification (Fig. 3.6, b). In this case, the ratio between polar and non-polar groups is 0.45. This ratio is more than two times higher, in comparison to the initial powder. Consequently, lower C/Al ratio and reduced amount of non-polar C–C groups indicates increased surface polarity [17] and improved surface wettability.

Deconvolution results of O1s peaks of initial and plasma modified Al powder are presented in Figures 3.7 a and b, respectively. O1s peak consists of three components: lattice oxygen (Al–O–Al), Al hydroxyl (Al–OH) and polar C–O groups. For the initial powders the peak area of Al hydroxyls (58.3 %) is higher than the Al–O–Al (mainly Al oxide) peak (38.4 %) (Fig. 3.7, a). After Al powder modification in plasma the peak area of Al hydroxyl groups sharply decreased to 18.0 % and area of Al–O–Al peak increased up to 71.3 % (Fig. 3.7, b). Surface adsorbed OH groups are very sensitive to the ions and electrons from plasma which can initiate OH desorption (electrons provide energy while H^+ ions bond to OH and desorb as H_2O molecules). Al/O terminated surface can enhance reactivity of Al with water. Moreover, amount of polar C–O groups increased more than three times from 3.3 % up to 10.7 % after plasma modification.

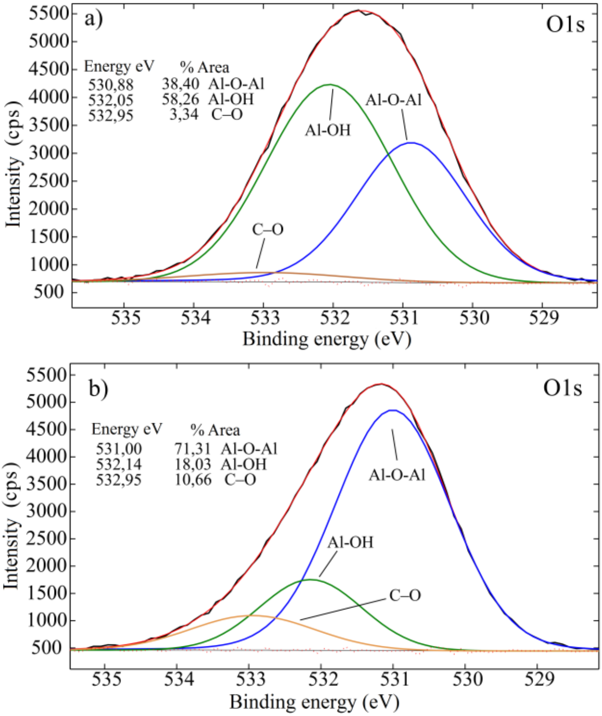

Fig. 3.7. O1s peak fitting of unmodified (a) and plasma modified (b) Al powder at 250 W, 8 cm for 1 h

High amount of Al hydroxyl groups at the surface increases the adsorption of non-polar molecules and surface hydrophobicity as well [19]. Therefore, this is an additional argument that after plasma treatment Al surface obtains higher wettability due to the reduced content of OH groups. It is well known that hydrogen plasma could be used as reactive gas for changing the top surface chemistry [20]. Hydrogen gas plasma consists of the highly reactive atomic hydrogen, ions and electron-excited H_2 molecules (2H, $2H^+$, H_2^*) [21] which can break up weak chemical bonds (e.g., OH groups) at the near surface or remove adventitious carbon [22]. It is noted that hydroxide layer could act as an additional barrier and diffusion resistance for water molecules [23], while increased surface wettability leads to better contact and more efficient reaction with water. Reconstruction of surface layer atoms and charge redistribution could be induced due to surface cleaning, introduction of small amount of hydrogen and relocation of excited atoms at the surface.

It is indicated that reactivity of metal oxide surfaces depends on the degree of surface hydroxylation [24]. Peter J. Eng et al. [24] showed that under normal atmospheric conditions (298 K and 50-60 % relative humidity) about 3 monolayers of water are adsorbed on alumina surface. A fully hydroxylated surface is oxygen-terminated layer with double Al layer below and laterally disordered layer approximately 2.3 Å above the surface [24]. This layer is related to adsorbed water and possibly could be a mixture of hydrogen-bonded water and adventitious carbon. Meanwhile clean alumina surface is Al-terminated or mixed Al/O-terminated surface. Such surface is highly reactive with water due to the undersaturation. Surface hydroxylation leads to significant surface relaxation with regard to hydrogen bonding. Saturated OH-terminated surface will have greatly decreased reactivity with water [24]. Because of this small atomic arrangement of outermost layer, aluminium surface becomes passivated and chemically inert (decreased surface energy). Moreover, the study by Gentleman and Ruud [25] showed that hydrophobicity is attributed to the increased hydroxylation of the surface.

Al–O-terminated surface was obtained after plasma activation process (Fig. 3.7, b). Such surface is likely to be energetically active and reacts with water very well due to high dipole moment and unsaturated surface bonds. In the case of reaction with water, Al surface will tend to bond with water molecules (dissociatively adsorb) and relax as soon as possible.

Figures 3.8 a and b show the Al 2p spectra for unmodified and plasma-modified Al powder, respectively. Two peaks were observed which are attributed to Al^0 (Al–Al) and Al^{3+} (Al–O–Al and Al–OH) states. After plasma treatment the Al^{3+}/Al^0 ratio increased from 2.16 (Fig. 3.8, a) up to 2.77 (Fig. 3.8, b) which indicates the formation of Al/O terminated surface and is in agreement with O 1s peak analysis (Fig. 3). Moreover, metallic Al^0 state slightly shifted to lower binding energy (from 71.7 to 71.5 eV) which indicated changes in chemistry (i.e.:

electrons density, structure of atoms in metallic state) of modified Al surface. This might be a fingerprint of vacancies and undercoordinated metallic structure [26]. As has been mentioned in the discussion of XRD and SEM results, hydrogen plasma can generate large amount of oxygen vacancies in a thin oxide layer and produce hydrogen–vacancies complexes which leads to the formation of open bonds (Al^{3+}) and unsaturated Al structure.

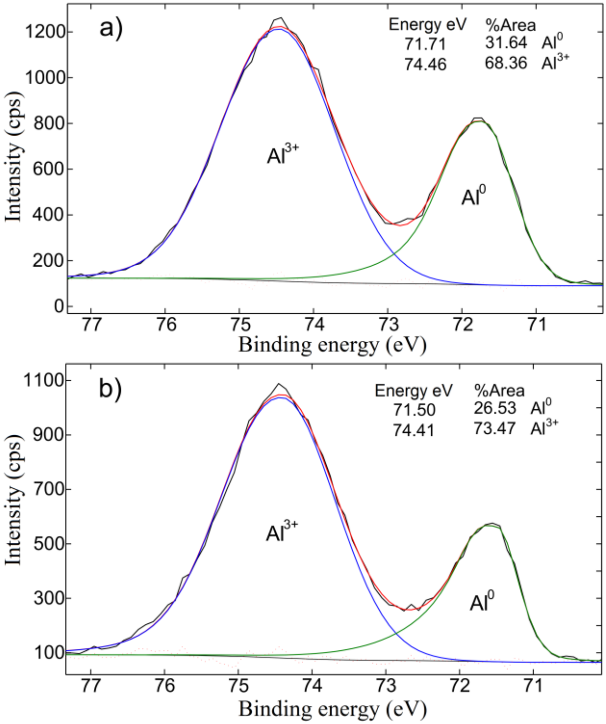

Fig. 3.8. Al2p peak fitting of unmodified (a) and plasma modified (b) Al powder at 250 W, 8 cm for 1 h

To sum up, hydrogen gas plasma initiates the following changes on the surface of Al powder:

1. Slightly changed surface morphology – formation of micro cracks, bubbles and irregularities, increase in BET surface area (weakened barrier oxide layer and improved surface adhesion);
2. Increase in free surface energy (improved Al activity);
3. Plasma surface cleaning removes organic compounds, OH groups and break down C–C bonds (hydrophilicity effect and improved Al activity);

4. Reduced amount of non-polar and increased amount of polar molecule groups on the surface (hydrophilicity effect and improved Al activity).
5. Formation of Al–O terminated surface which is reactive with water.
6. Possible formation of vacancies and undercoordinated Al structures (open bonds) in the oxide barrier layer and at the Al–oxide interface which leads to the increased reactivity of Al powder with water.

3.5. Hydrogen production after reaction between aluminium powder and water

Hydrogen production using reaction between plasma activated Al powder and water, and reaction kinetics were investigated in 4 different cases: influence of plasma activation parameters; effect of water temperature; influence of sodium hydroxide amount; and effect of water amount used during the reaction. These factors have an effect on hydrogen synthesis and are mostly investigated in the literature using activated aluminium by other methods.

3.5.1. Influence of plasma activation conditions on hydrogen synthesis

Reactivity of modified Al powder in water was tested immediately after plasma activation and hydrogen yield after reaction with water is presented in Fig. 3.9. Hydrogen production was measured for samples modified under altered activation conditions. Reaction was performed using 0.05 g of aluminum powder with 40 ml of water at room temperature of 23–25 ºC. Plasma modified Al powder showed the increased hydrophilicity and sank in water immediately after it reached the water surface. The small amount of 0.2 g sodium hydroxide (as reaction promoter) was dissolved in 100 ml of distilled water resulting 0.05 M NaOH (molar concentration).

Plasma treatment decreased the concentration of OH groups and created Al/O-terminated surface. Furthermore, Liu et. al. noted that water molecules dissociatively adsorb at the defect sites of Al surface oxide [27].

Reaction behavior and the total amount of hydrogen produced are practically similar for all tested samples despite the conditions of plasma activation (power – 250 W, distance between sample and magnetron – 4 cm and 8 cm, activation time – 1 h and 3 h). Maximum amount of hydrogen 60 ml ± 2 was produced in 619–740 seconds (Fig. 3.9). It means that 96 % of total theoretical hydrogen yield (1245 ml) could be reached.

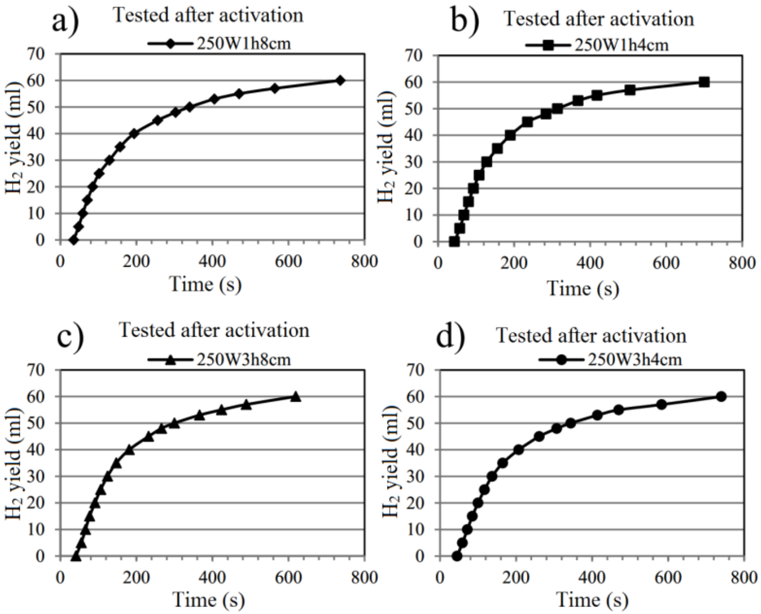

Fig. 3.9. Hydrogen generation tested straight after plasma activation using 40 ml of water at temperature room temperature

Ageing test showed that plasma modified aluminum powder remained highly reactive and easily reached 60 ml ± 2 ml amount of hydrogen in 743-786 seconds even after 6 months of storage (Fig. 3.10). Of course, it needs to be mentioned that activated Al powder was stored in a closed vessel, avoiding the interaction with the environment.

Compared to the Al powder tested immediately after activation, reaction started almost at the same time. However, the time of reaction when 60 ml of hydrogen was produced, increased up to 40–132 seconds.

To sum up, hydrogen yield and kinetics did not depend on the mentioned plasma activation parameters (ionic current density 0.5 or 1.1 mA/cm^2), while aging had only a modest effect on Al powders.

It is worth to mention that when activated Al powder is stored in an open container and allowed to interact with ambient air, the hydrophilic surface of modified Al powder transforms to the hydrophobic. Perhaps surface undergoes the relaxation due to interaction with moisture and carbon compounds in the ambient air.

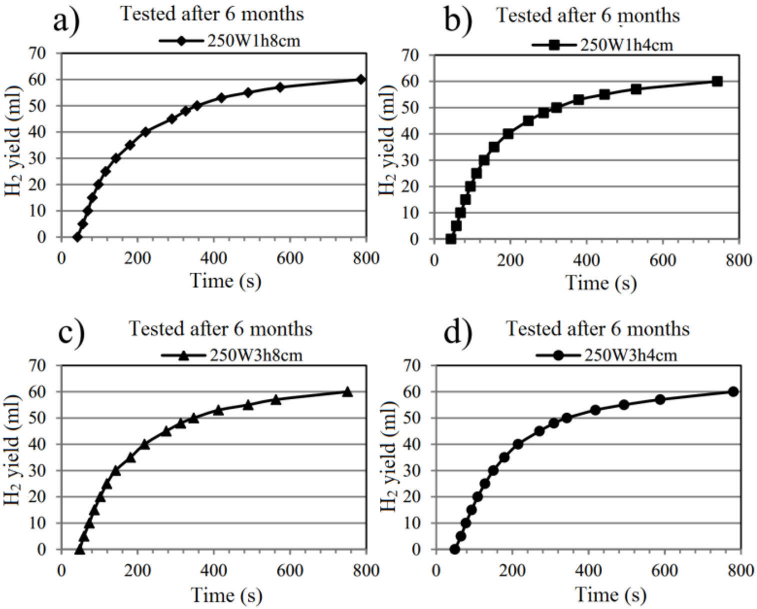

Fig. 3.10. Hydrogen generation tested after 6 months of storage using plasma modified Al powder and 40 ml of water at room temperature

3.5.2. Effect of water temperature on the kinetics of hydrogen generation

The yield of hydrogen produced (H_2 yield vs. time) after unmodified and plasma modified Al powder reaction with water is presented in Fig. 3.11 a and b shows enlarged view of the reaction start. Small amount of sodium hydroxide (0.2g of NaOH) was dissolved in 100 ml of pure water in order to increase the concentration of OH groups slightly. The reaction was tested using 40 ml of water (with dissolved NaOH) at different initial temperatures (25°C, 30°C, 35°C and 40°C) reacting with 0.05 g Al powder.

Modified Al powder sank immediately after immersion into the water because of plasma induced hydrophilicity while unmodified Al powder floated on the top of water. The insight images show water drops placed on unmodified and plasma modified Al powder where contact angle drastically decreased from 121° ± 5° to 38° ± 5° (Fig. 3.11, a). Change of cumulative H_2 yield with increasing temperature was negligible in both cases. Modified Al powder produced 63 ml ± 2 ml of H_2 at 25°C of initial water temperature and 66 ml ± 2 ml at 40°C, whereas H_2 yield of unmodified Al rised from 15 ml ± 2 ml to 20 ml ± 2 ml increasing temperature from 25°C to 40°C, respectively (Fig. 3.11, a). It is clearly seen (Fig. 3.11, b), that induction time (until H_2 generation starts) is decreased from 44 s to 13 s for modified and from 190 s to 95 s for unmodified Al at water temperatures of 25°C and 40°C, respectively. Increasing the initial reaction temperature results in enhanced Al-water reaction and higher H_2 flow rate. Also it was observed that Al corrosion is very slow in cold water.

Al-water reaction is highly exothermic which increase water temperature during the reaction as well: $Al + 3H_2O \rightarrow Al(OH)_3 + 1.5H_2 + 426.5$ kJ [28].

According to these results, it can be concluded that initial water temperature did not affect the produced hydrogen amount but has significant effect on the reaction kinetics. Water molecules reach metal aluminium faster at higher temperatures because aluminium oxide layer becomes more loosely (opening more pathways for water molecules). Also higher temperature increases diffusion rate of OH^- ions through the oxide layer to the metallic Al.

Lowering the H_2 production temperature is important for portable fuel cell system designers.

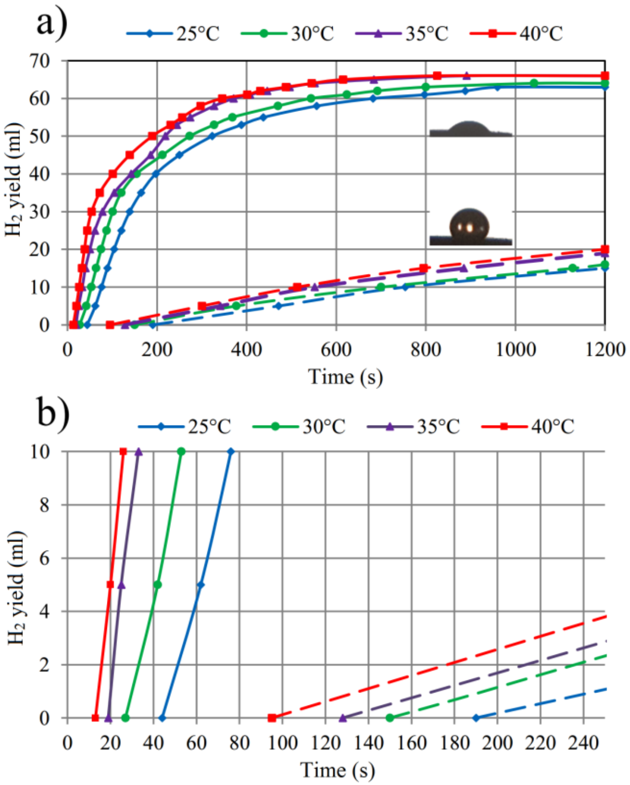

Fig. 3.11. Temperature influence on H_2 generation using 0.05 g of modified and unmodified Al powder with 40 ml of water (0.2 g of NaOH dissolved in 100 ml H_2O) (a) and enlarged view of reaction start (b)

3.5.3. Influence of sodium hydroxide amount on hydrogen generation

Hydrogen generation using 0.05 g of Al powder with different NaOH concentration (0.12 g, 0.24 g and 0.43 g) dissolved in 50 ml of pure water is presented in Fig. 3.12. Different molar concentrations of 0.06 M, 0.12 M and 0.43 M, were achieved with increasing amount of NaOH. Reactions started after 48 s, 35 s and 22 s using 0.12 g, 0.24 g and 0.43 g of NaOH, respectively. Generated volume of H_2 slighlty increased from 60 ml ± 2 ml up to 64 ml ± 2 ml with increasing molar concentration. Reaction was accelerated and hydrogen production rate increased as well. Modified Al powder reacted completely after 745 s, 556 s and 384 s, respectively. Mobile OH^- ions can migrate along the Al_2O_3 surface of plasma-modified Al and damage it even more creating more pathways for water molecules.

However, large amount of sodium hydroxide results corrosive environment and should be avoided. Hydrogen produced and supplied to the fuel cell under such conditions can eventually damage the proton exchange membrane.

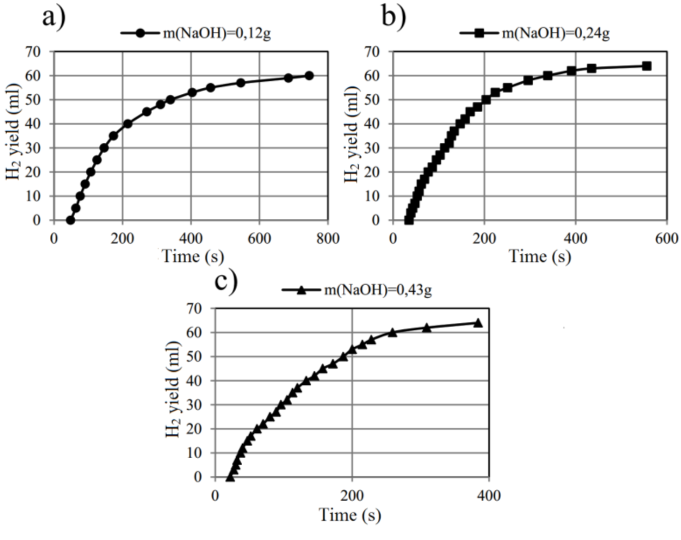

Fig. 3.12. Hydrogen production using 0.05 g of Al powder with different amount of sodium hydroxide dissolved in 50 ml of water: 0.12 g (a), 0.24 g (b) and 0.43 g (c)

3.5.4. Influence of water amount on the hydrogen generation

Fig. 3.13 shows hydrogen production yield after reaction between 0.05 g of Al powder and different volume of water (from 10 ml to 100 ml). In all cases slighlty alkaline water solution (0.05M NaOH) at temperature of 25 ºC was used.

The reaction started after 75 s, 88 s and 82 s using 10, 20 and 30 ml of water, respectively. Meanwhile, reaction began in less than 1 minute after powder immersion using 40, 50 and 100 ml of water. Hydrogen production yield was 17, 29, 40, 60, 61 and 63 ml ± 2 ml with increasing the water volume from 10 up to 100 ml, respectively. In the cases of small amounts of water (10, 20 and 30 ml), activated Al powder completely reacted with water and produced 50–60 ml ± 2 ml of hydrogen after 24 hours approximately. Such reduced reaction kinetics could be determined by two reasons: (1) less water with the same amount of Al powder means less OH groups which can disrupt aluminum oxide layer and maintain the reaction; (2) reaction kinetics could be reduced by the by-product generated during Al-water reaction, which mixes with pure Al powder and covers the surface by creating an additional barrier.

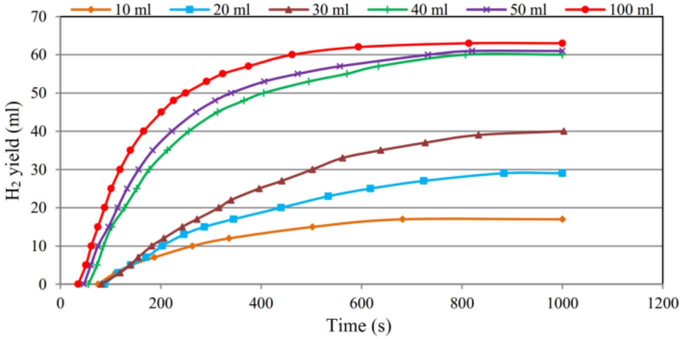

Fig. 3.13. Hydrogen production using 0.05 g of Al powder and different volume of water (10 ml, 20 ml, 30 ml, 40 ml, 50 ml and 100 ml)

3.5.5. Aluminium-water reaction mechanism

Water molecules can be dissociatively adsorbed ($2H_2O \rightarrow 2OH + H_2 \uparrow$) on the defect sites found in modified Al surface. During the Al-water reaction counter diffusion of ions through the modified oxide barrier layer may occur. Metal cations (Al^{3+}) migrate outwards across the oxide layer while OH^- ions migrate inward from the water (Fig. 3.14). The migration of ions is assisted by the high self-generated electric field in thin oxide layer (could reach up to 10^7 V/cm) which is created between negative ions on the outer layer and positive ions at the interface of Al–oxide. Mobile OH^- ions diffuse by oxygen vacancies in the oxide layer. Therefore, large amount of vacancies created by hydrogen plasma treatment induce effective diffusion of hydroxide ions (as well water molecules) through the barrier.

At the beginning of Al-water reaction, hydrogen accommodates at the interface of Al-oxide while critical pressure is reached and hydrogen gas is released. Consequently oxide layer is disrupted and metallic Al surface is fully opened to water molecules leading to increased reaction rate.

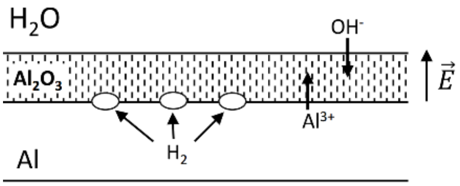

Fig. 3.14. Reaction mechanism

3.6. Electricity generation using proton exchange membrane fuel cell

Application of in situ hydrogen generation using Al/water reaction in proton exchange membrane (PEM) fuel cell is very attractive due to low working temperature and non-hazardous by-product. Fig. 3.15 shows the voltage generated by PEM fuel cell during hydrogen evolution using plasma modified Al/water reaction.

In this case, power generation starts shortly as aluminum-water reaction begins and an appropriate stable hydrogen flow is reached. Measurements were performed at different temperature points (25 ºC and 35 ºC) using 0.1 g of modified Al powder and 40 ml of water. Molar concentration of sodium hydroxide dissolved in distilled water ranged from 0.025 M to 0.1 M. It is clearly seen that the longest steady voltage generation was obtained using 0.1 M of NaOH (Fig. 3.15, a and b), while the lowest promoter concentration leads to unstable voltage generation due to insufficient hydrogen flow rate (Fig. 3.15, a). The generated voltage reached 1.2 V after 30 s using 0.05 M and 0.1 M NaOH and after 100 s using 0.025 M NaOH at temperature of 25 ºC. Fast start-up of the fuel cell is one of the essential properties.

Hydrogen generation rate caused the change of voltage values during the experiment. As the hydrogen flow rate decreased, the voltage of the fuel cell decreased as well. Raised initial water temperature (Fig. 3.15, b) leads to increased H_2 flow rate which results slightly higher voltage value (1.3 V) achieved after 15-20 s (Fig. 3.15, b). However, shorter electricity generation was registered. Additionally, it is worth to be mentioned that concentration of alkali should be kept as low as possible due to degeneration of PEM fuel cell membrane.

When hydrogen is provided to the fuel cell, a contollable H_2 flow rate is generally required for stable power generation. Control of reaction temperature, amount of OH^- ions and reactant could regulate the produced hydrogen flow and reaction rate. The energy generated by PEM fuel cell was measured appoximately 25, 50 and 70 mWh at 25°C and 20, 35 and 47 mWh at 35 °C using 0.025 M, 0.05 M and 0.1 M, respectively. Thus the best result is 0.7 Wh / 1 g Al. This value could be increased using a suitable reaction vessel and controlling the hydrogen flow supplied to the fuel cell. Such technology could ensure safe and continious power generation for portable electronic devices.

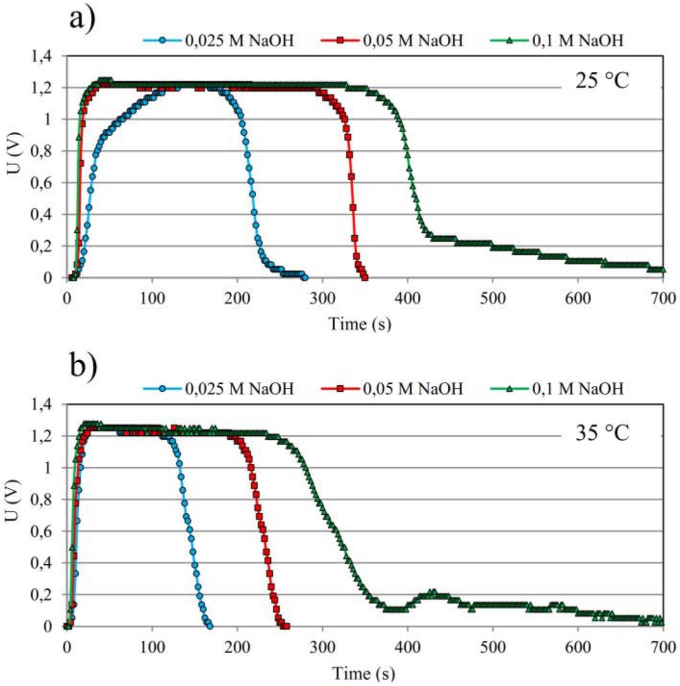

Fig. 3.15. Electricity generation by PEM fuel cell after plasma modified Al powder reacted with 40 ml of water under different concentrations of NaOH at initial temperatures of (a) 25°C and (b) 35°C

3.7. Synthesis of γ-aluminium oxide powder

By-product of Al-water reaction could be used as a precursor for γ-Al_2O_3 synthesis. In order to avoid additional impurities, plasma modified Al powder reacted with distilled water at temperature of 40 ºC, which led to increased reaction kinetics.

SEM was performed to investigate the surface morphology of dried by-product (Fig. 3.16, a and b) obtained after the aluminium/water reaction and the gamma alumina (Fig. 3.16 c and d) synthesised using heat pre-treatment. The surface morphology was similar during the transformations of the aluminium/water reaction by-product into the boehmite and γ-Al_2O_3 phases. The SEM images (Fig. 3.16; scale bar represents 100 μm) indicate agglomerations of the powder particles, which formed larger, irregularly shaped aggregates. The higher-magnification images (Fig. 3.16; scale bar represents 3 μm) reveal a porous surface where pores were connected to each other in all cases. Thus, large BET surface area is expected which is an important factor for the catalytic properties of γ-Al_2O_3.

The EDS results confirmed the presence of oxygen, aluminium, and a small amount of carbon in all the samples. No additional chemical impurities were detected. The oxygen/aluminium ratio decreased from 3.36 for the aluminium/water by-product to 2.05 for gamma alumina because of the dehydroxylation that occurred during heat pre-treatment.

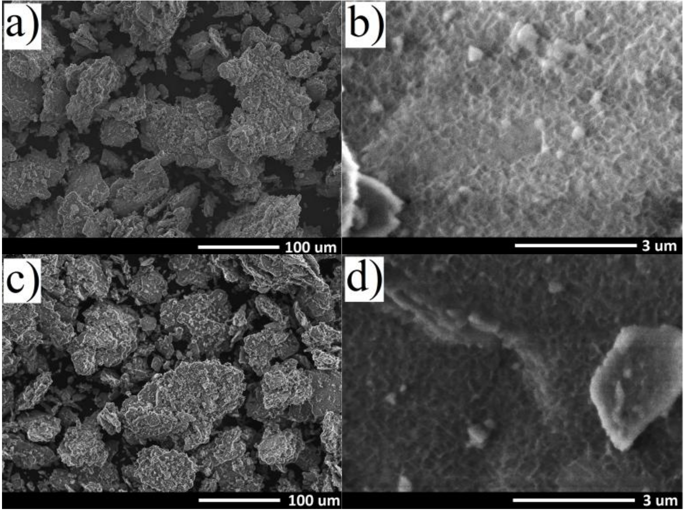

Fig. 3.16. SEM images of the initial by-product (mainly $Al(OH)_3$) surface obtained after the aluminium/water reaction (a–b) and the gamma alumina surface obtained after the aluminium hydroxide was heated at 500 °C (c–d)

The XRD analysis identifies the pure by-product of the aluminium/water reaction and the phase transition induced by the heat treatment. It indicates (Fig. 3.17, a) that the by-product obtained after the reaction between the plasma-modified aluminium and water was a mixture of aluminium hydroxide ($Al(OH)_3$), boehmite (AlO(OH)), and a small amount of pure aluminium. Clearly, monoclinic $Al(OH)_3$ (space group symmetry P21/a) was the predominant compound, with a crystallite size of 59.7 nm ± 2 nm. A small amount of pure aluminium was detected because of incomplete exothermic aluminium/water reaction.

The gamma alumina phase was synthesised via the thermal dehydration of boehmite at 500 °C (Fig. 3.17, b). The desorption of surface hydroxyl groups and the loss of structural water led to the formation of γ-Al_2O_3 with a spinel-like face-centred cubic structure (space group symmetry Fd-3m). The boehmite and aluminium peaks fully disappeared after the synthesis of the new phase. The XRD pattern was composed of several small and three well-defined diffraction peaks of γ-Al_2O_3 at 31.7°, 37.5°, 39.2°, 45.7°, 60.6°, and 66.7°, which correspond to the (220), (311), (222), (400), (511), and (440) reflections, respectively. The broadened peaks suggest that the synthesised product remained nanocrystalline.

The calculated mean crystallite size was 5.2 nm ± 1 nm. Additional broadening of peaks could be associated with the presence of defects. The XRD analysis does not reveal any characteristic peaks of new compounds, indicating high purity of the produced gamma alumina.

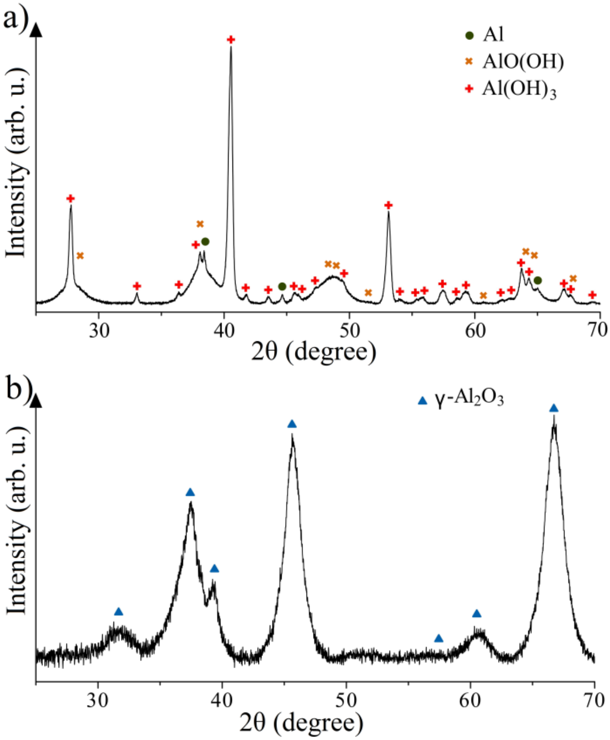

Fig. 3.17. XRD results for the by-product obtained after the reaction between the modified aluminium powder and distilled water (a) and the complete transformation of aluminium hydroxide into gamma alumina after heating at 500 °C (b)

The XPS spectra (Fig. 3.18) indicate the presence of carbon (C1s), oxygen (O1s), and aluminium (Al2p) on the surfaces of the initial by-product and the final product (gamma alumina). No impurities were detected; even on the nanoscale (depth and diameter of the measurement area were up to 10 nm and 100 μm, respectively). The carbon originated mainly from hydrocarbon that was desorbed during thermal treatment, resulting in the reduction of C1*s* from 8.2 to 3.1 at.%. The oxygen concentration decreased from 68.8 to 64.9 at.%, while the amount of aluminium greatly increased from 23 to 32.8 at.%. A deficiency of aluminium (actual ratio of Al2p/O1s = 0.51 vs. stoichiometric ratio of Al2p/O1s = 0.66) was observed on the surface of the gamma alumina, which may be related to the creation of cationic Al^{3+} vacancies and/or deviation induced by carbon amount.

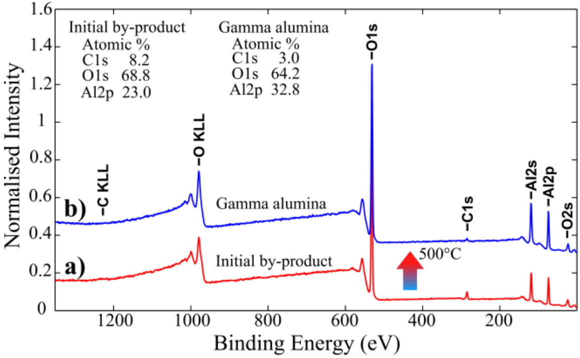

Fig. 3.18. XPS surface elemental composition analysis for the initial by-product obtained after the aluminium/water reaction (a) and the gamma Al_2O_3 formed after the high-temperature treatment of the reaction by-product at 500 °C (b)

One of the most important parameters for high catalyst activity is a specific surface area, which depends on the amount of coordinatively unsaturated sites. Active catalytic species can be effectively dispersed on such a large specific surface area. The specific surface area of 206.8 m^2g^{-1} obtained after the aluminium/water reaction increased to 247.9 m^2g^{-1} after the gamma-alumina synthesis. This increase in the surface area corresponds to the decrease of the nanocrystallite size (XRD results).

To sum up, nanocrystalline gamma alumina with a high purity and large specific surface area was successfully synthesised via the reaction between plasma-activated aluminium metal and water. The level of remaining impurities is negligible because the purity of the obtained gamma alumina depends only on the purity of initial aluminium powders, the working gasses used in the activation procedure, and distilled water. The price of manufacturing γ-Al_2O_3 can be lowered because of the production of high-purity H_2, which can be used for high-efficiency generation of electrical energy, offering environmental benefits. About 2g of γ-Al_2O_3 is received after 1 g of Al reacted with water.

CONCLUSIONS

In this thesis, a naturally formed amorphous oxide layer on Al surface, which prevents reaction with water, was modified under low-temperature plasma treatment and analysed in order to find out the mechanism of Al activation. Generated hydrogen yield was determined during the experimental investigation, altering the reaction temperature, amount of NaOH and water volume. Transformation of reaction by-product to the product for secondary-use was performed.

1. It has been experimentally found that plasma activation is effective using magnetron with Al target. Hydrogen plasma parameters: H_2 gas pressure 13 Pa, $I = 1$ A ($P = 250$ W), distance x between the magnetron and the sample 4 cm $\leq x \leq$ 8 cm (plasma becomes unstable at a shorter than 4 cm distance), ionic current density from 0.5 up to 1.1 mA/cm^2, activation time – form 1 to 3 hours. Whereas, activation of Al powder is not uniform using electrodes as plasma generator instead of magnetron.
2. Hydrophobic Al powder surface turns into hydrophilic because plasma changes only structure of the surface with decreasing amount of nonpolar molecules and increasing amount of polar molecules groups (XPS analysis). Ratio of polar/nonpolar molecules groups increased from 0.21 up to 0.45 after plasma activation. The reduction of OH groups (from 58 % to 18 %) and formation of Al–O terminated surface also has a positive effect on the Al reactivity in water (XPS and gas analyser). Inhomogeneously distributed defects were observed by SEM. Meanwhile XRD did not identify any significant structural changes. Also this technology can be applied for MgH_2 synthesis.
3. Modified Al powder can produce about 96 % of theoretical hydrogen yield (1200 ml ± 2 ml / 1 g Al). Al-water reaction efficiency and kinetics are improved with increasing water temperature from 25 °C up to 40 °C, but reaction becomes very passive at the temperature below 15 °C. The ratio of Al/H_2O is also an important factor (0.05 g Al + 40 ml H_2O, it is the minimum amount of water required for the complete Al reaction in the shortest time).
4. Al-water reaction is suitable for electricity generation using proton exchange membrane fuel cell. A PEM fuel cell (nominal power of 1.5 W) with a load of 2 Ω can generate about 0.7 Wh of electricity using hydrogen produced after fully reacted 1 g of modified aluminium with water at temperature of 25 °C.
5. Boehmite (AlO(OH)) was synthesised after Al-water reaction by-product was heated up at 280 °C under atmospheric conditions. While the nanocrystalline γ-Al_2O_3 was received after boehmite was heated up at 500 °C. BET surface area of γ-Al_2O_3 is 247.9 m^{2}g^{-1} and crystallite size – 5.2 nm. Additional

impurities were not registered by XRD and XPS analysis, which indicates that especially pure γ-Al_2O_3 was synthesised.

REFERENCES

[1] A. Fridman, Plasma chemistry, Cambridge University Press, Cambridge, 2008.

[2] I.P. Jain, C. Lal, A. Jain, Hydrogen storage in Mg : A most promising material, Int. J. Hydrogen Energy. 35 (2010) 5133–5144. doi:10.1016/j.ijhydene.2009.08.088.

[3] D. Milcius, J. Grbović-Novaković, R. Zostautiene, M. Lelis, D. Girdzevicius, M. Urbonavicius, Combined XRD and XPS analysis of ex-situ and in-situ plasma hydrogenated magnetron sputtered Mg films, J. Alloys Compd. 647 (2015) 790–796. doi:10.1016/j.jallcom.2015.05.151.

[4] C.E. Buckley, H.K. Birnbaum, Characterization of the charging techniques used to introduce hydrogen in aluminum, J. Alloys Compd. 330–332 (2002) 649–653. doi:10.1016/S0925-8388(01)01496-7.

[5] C.E. Buckley, H.K. Birnbaum, J.S. Lin, S. Spooner, D. Bellmann, P. Staron, E. Hollar, Characterization of H defects in the aluminium – hydrogen system using small-angle scattering techniques research papers Characterization of H defects in the aluminium ± hydrogen system using small-angle scattering techniques, J. Appl. Crystallogr. 34 (2001) 119–129.

[6] D. Xie, S. Li, M. Li, Z. Wang, P. Gumbsch, J. Sun, E. Ma, J. Li, Z. Shan, Hydrogenated vacancies lock dislocations in aluminium, Nat. Commun. 7 (2016) 1–7. doi:10.1038/ncomms13341.

[7] J. Graetz, J.J. Reilly, V.A. Yartys, J.P. Maehlen, B.M. Bulychev, V.E. Antonov, B.P. Tarasov, I.E. Gabis, Aluminum hydride as a hydrogen and energy storage material : Past , present and future, J. Alloys Compd. 509 (2011) S517–S528. doi:10.1016/j.jallcom.2010.11.115.

[8] A. Zaluska, L. Zaluski, J.O. Strom-Olsen, Nanocrystalline magnesium for hydrogen storage, J. Alloys Compd. 288 (1999) 217–225. doi:10.1016/S0925-8388(99)00073-0.

[9] F.M. Chang, S.L. Cheng, S.J. Hong, Y.J. Sheng, H.K. Tsao, Superhydrophilicity to superhydrophobicity transition of CuO nanowire films, Appl. Phys. Lett. 96 (2010) 114101-1-114101–3.

[10] M. Li, D. Xie, E. Ma, J. Li, X. Zhang, Z. Shan, Effect of hydrogen on the integrity of aluminium–oxide interface at elevated temperatures, Nat. Commun. 8 (2017) 1–7. doi:10.1038/ncomms14564.

[11] D. Milcius, L.L. Pranevicius, C. Templier, Hydrogen storage in the bubbles formed by high-flux ion implantation in thin Al films, J. Alloys Compd. 398 (2005) 203–207. doi:10.1016/j.jallcom.2005.02.003.

[12] D.-G. Xie, Z.-J. Wang, J. Sun, J. Li, E. Ma, Z.-W. Shan, In situ study of

the initiation of hydrogen bubbles at the aluminium metal/oxide interface, Nat. Mater. 14 (2015) 1–6. doi:10.1038/nmat4336.

[13] P. Swift, Adventitious carbon-the panacea for energy referencing?, Surf. Interface Anal. 4 (1982) 47–51. doi:10.1002/sia.740040204.

[14] D.J. Miller, M.C. Biesinger, N.S. McIntyre, Interactions of CO2 and CO at fractional atmosphere pressures with iron and iron oxide surfaces: One possible mechanism for surface contamination?, Surf. Interface Anal. 33 (2002) 299–305. doi:10.1002/sia.1188.

[15] H. Piao, N.S. McIntyre, Adventitious carbon growth on aluminium and gold-aluminium alloy surfaces, Surf. Interface Anal. 33 (2002) 591–594. doi:10.1002/sia.1425.

[16] I. Bertoti, M. Mohai, P.H. Mayrhofer, C. Mitterer, Surface chemical changes induced by low-energy ion bombardment in chromium nitride layers, Surf. Interface Anal. 34 (2002) 740–743.

[17] J. Long, M. Zhong, H. Zhang, P. Fan, Superhydrophilicity to superhydrophobicity transition of picosecond laser microstructured aluminum in ambient air, J. Colloid Interface Sci. 441 (2015) 1–9. doi:10.1016/j.jcis.2014.11.015.

[18] G. Azimi, R. Dhiman, H. Kwon, A.T. Paxson, K.K. Varanasi, Hydrophobicity of rare-earth oxide ceramics, Nat. Mater. 12 (2013) 315–320. doi:10.1038/nmat3545.

[19] S. Takeda, M. Fukawa, Y. Hayashi, K. Matsumoto, Surface OH group governing adsorption properties of metal oxide films, Thin Solid Films. 339 (1999) 220–224. doi:10.1016/S0040-6090(98)01152-3.

[20] N. Korner, E. Beck, A. Dommann, N. Onda, J. Ramm, Hydrogen plasma chemical cleaning of metallic substrates and silicon wafers, Surf. Coatings Technol. 76–77 (1995) 731–737. doi:10.1016/0257-8972(95)02503-0.

[21] K.C. Sabat, P. Rajput, R.K. Paramguru, B. Bhoi, B.K. Mishra, Reduction of Oxide Minerals by Hydrogen Plasma : An Overview, Plasma Chem Plasma Process. 34 (2014) 1–23. doi:10.1007/s11090-013-9484-2.

[22] U. Kafader, H. Sirringhaus, H. von Känel, In situ DC-plasma cleaning of silicon surfaces, Appl. Surf. Sci. 90 (1995) 297–302. doi:10.1016/0169-4332(95)00166-2.

[23] P. Dupiano, D. Stamatis, E.L. Dreizin, Hydrogen production by reacting water with mechanically milled composite aluminum-metal oxide powders, Int. J. Hydrogen Energy. 36 (2011) 4781–4791. doi:10.1016/j.ijhydene.2011.01.062.

[24] P. Eng, T. Trainor, G. Brown, G. Waychunas, M. Newville, S. Sutton, M. Rivers, Structure of the hydrated – Al2O3 (0001) surface, Science (80-.).

288 (2000) 1029–1033. doi:10.1126/science.288.5468.1029.

[25] M.M. Gentleman, J.A. Ruud, Role of hydroxyls in oxide wettability, Langmuir. 26 (2010) 1408–1411. doi:10.1021/la903029c.

[26] G. Maidecchi, C.V. Duc, R. Buzio, A. Gerbi, G. Gemme, M. Canepa, F. Bisio, Electronic structure of core-shell metal/oxide aluminum nanoparticles, J. Phys. Chem. C. 119 (2015) 26719–26725.

[27] Q. Liu, X. Tong, G. Zhou, H2O dissociation-induced aluminum oxide growth on oxidized Al(111) surfaces, Langmuir. 31 (2015) 13117–13126.

[28] H. Dai, G. Ma, X. Kang, P. Wang, Hydrogen generation from coupling reactions of sodium borohydride and aluminum powder with aqueous solution of cobalt chloride, Catal. Today. 170 (2011) 50–55. doi:10.1016/j.cattod.2010.10.094.

PUBLICATIONS RELATED TO THE DISSERTATION

Publications in the journals of „Clarivate Analytics – Web of Science Core Collection“

1. Milčius, Darius; Žostautienė, Rasa; Lelis, Martynas; Grbović-Novaković, Jasmina; Girdzevičius, Dalius; Urbonavičius, Marius. Combined XRD and XPS analysis of ex-situ and in-situ plasma hydrogenated magnetron sputtered Mg films // Journal of Alloys and Compounds. ISSN 0925-8388. 2015. Vol.647, p. 790–796.
2. Lesnicenoks, Peteris; Zemitis, Janis; Grinberga, Liga; Chikvaidze, George; Kleperis, Janis; Urbonavičius, Marius; Tučkutė, Simona; Milčius, Darius. Modified graphene sheet stacks for hydrogen binding // Material Science (Medžiagotyra). ISSN 1392-1320. 2017. Vol. 23, No. 1, p. 3–5.
3. Urbonavičius, Marius; Varnagiris, Šarūnas; Milčius, Darius. Generation of hydrogen by the reaction between plasma modified aluminium and water // Energy Technology. ISSN 2194–4296. 2017. Vol. 5, No. 12, p. 2300-2308.

Articles in other scientific journals

1. Urbonavičius, Marius; Milčius, Darius. Reaction of aluminum with water to produce hydrogen // 5th International Conference of Radiation Interaction with Materials: Fundamentals and Applications 2014. Kaunas, Lithuania, May 12-15, 2014. ISSN 2351-583X, p. 190-193.
2. Urbonavičius, Marius; Tučkutė, Simona; Varnagiris, Šarūnas; Lelis, Martynas; Milčius, Darius. Temperatūros įtaka aliuminio ir vandens reakcijų kinetikai išgaunant vandenilį, skirtą mažos galios prietaisams // Energetika. ISSN 0235-7208. 2016. T.62, Nr. 3, p. 145–154.
3. Urbonavičius, Marius; Varnagiris, Šarūnas; Girdzevičius, Dalius; Milčius, Darius. Hydrogen generation based on aluminum-water reaction for fuel cell applications // Energy Procedia. ISSN 1876-6102. 2017. Vol. 128, p. 114-120.
4. Girdzevičius, Dalius; Urbonavičius, Marius; Varnagiris, Šarūnas; Milčius, Darius. Implementation of hydrogen plasma activation of Mg powder in two steps hydrogenation // Energy Procedia. ISSN 1876-6102. 2017. Vol. 128, p. 108-113.

Publications in the international conferences

1. Urbonavičius, Marius; Milčius Darius. Hydrogen generation from reaction between plasma activated aluminum powder and water // 11th International Conference of Young Scientists on Energy Issues (CYSENI 2014): Kaunas, Lithuania, May 29-30, 2014. Kaunas: LEI, 2014. ISSN 1822-7554, p. I-1–I-8.

2. Urbonavičius, Marius; Milčius, Darius. Reaction between plasma activated aluminium powder and water under various conditions // 12th International Conference of Young Scientists on Energy Issues (CYSENI 2015): Kaunas, Lithuania, May 27-28, 2015. Kaunas: LEI, 2015. ISSN 1822-7554, p. I-18–I-25.
3. Urbonavičius, Marius; Milčius, Darius. Power generation by proton exchange membrane fuel cell using plasma modified aluminum and water reaction // 13th International Conference of Young Scientists on Energy Issues (CYSENI 2016): Kaunas, Lithuania, May 26-27, 2016. Kaunas: LEI, 2016. ISSN 1822-7554, p. I-1–I-8.
4. Girdzevičius, Dalius; Milčius, Darius; Urbonavičius, Marius; Varnagiris, Šarūnas. Attempt to regenerate MgO to Mg under hydrogen plasma conditions // 14th International Conference of Young Scientists on Energy Issues (CYSENI 2017): Kaunas, Lithuania, May 25-26, 2017. Kaunas: LEI, 2017. ISSN 1822-7554, p. V-192–V-198.
5. Urbonavičius, Marius; Girdzevičius, Dalius; Varnagiris, Šarūnas; Milčius, Darius. Possible reduction of aluminium hydroxide in hydrogen gas plasma // 14th International Conference of Young Scientists on Energy Issues (CYSENI 2017): Kaunas, Lithuania, May 25-26, 2017. Kaunas: LEI, 2017. ISSN 1822-7554, p. V-180 – V-185.

Presentations at international conferences

1. Urbonavičius, Marius; Milčius, Darius. Reaction of aluminum with water to produce hydrogen // 5th International Conference of Radiation Interaction with Materials: Fundamentals and Applications 2014. Kaunas, Lithuania, May 12-15, 2014.
2. Urbonavičius, Marius; Milčius Darius. Hydrogen generation from reaction between plasma activated aluminum powder and water // 11th International Conference of Young Scientists on Energy Issues (CYSENI 2014): Kaunas, Lithuania, May 29-30, 2014. Kaunas: LEI, 2014. ISSN 1822-7554, p. I-1–I-8.
3. Lelis, Martynas; Urbonavičius, Marius; Milčius, Darius. Combined XRD and XPS analysis of in-situ plasma hydrogenated magnetron sputtered Mg films // 14th European Powder Diffraction Conference, Aarhus, Denmark, June 15-18, 2014.
4. Urbonavičius, Marius; Milčius, Darius. Hydrogen production by reacting activated aluminum metal with water // 9th International Scientific

Conference The Vital Nature Sign, Kaunas, Lithuania, May 14-16, 2015. ISSN 2335-8653. p. 109.

5. Girdzevičius, Dalius; Milčius, Darius; Urbonavičius, Marius. Plasma based ex-situ and in-situ hydrogenation of Mg films // 9th international scientific conference The Vital Nature Sign, Kaunas, Lithuania, May 14-16, 2015. ISSN 2335-8653, p. 103.
6. Urbonavičius, Marius; Milčius, Darius. Reaction between plasma activated aluminium powder and water under various conditions // 12th International Conference of Young Scientists on Energy Issues (CYSENI 2015): Kaunas, Lithuania, May 27-28, 2015. Kaunas: LEI, 2015. ISSN 1822-7554, p. I-18–I-25.
7. Urbonavičius, Marius; Milčius, Darius. Power generation by proton exchange membrane fuel cell using plasma modified aluminum and water reaction // 13th International Conference of Young Scientists on Energy Issues (CYSENI 2016): Kaunas, Lithuania, May 26-27, 2016. Kaunas: LEI, 2016. ISSN 1822-7554, p. I-1–I-8.
8. Girdzevičius, Dalius; Urbonavičius, Marius; Varnagiris, Šarūnas; Milčius, Darius. Implementation of hydrogen plasma activation of Mg powder in two steps hydrogenation // Conference of Environmental and Climate Technologies (CONECT 2017): Riga, Latvia, May 10-12, 2017.
9. Urbonavičius, Marius; Varnagiris, Šarūnas; Girdzevičius, Dalius; Milčius, Darius. Hydrogen generation based on aluminum-water reaction for fuel cell applications // Conference of Environmental and Climate Technologies (CONECT 2017): Riga, Latvia, May 10-12, 2017.
10. Girdzevičius, Dalius; Milčius, Darius; Urbonavičius, Marius; Varnagiris, Šarūnas. Attempt to regenerate MgO to Mg under hydrogen plasma conditions // 14th International Conference of Young Scientists on Energy Issues (CYSENI 2017): Kaunas, Lithuania, May 25-26, 2017. Kaunas: LEI, 2017. ISSN 1822-7554, p. V-192–V-198.
11. Urbonavičius, Marius; Girdzevičius, Dalius; Varnagiris, Šarūnas; Milčius, Darius. Possible reduction of aluminium hydroxide in hydrogen gas plasma // 14th International Conference of Young Scientists on Energy Issues (CYSENI 2017): Kaunas, Lithuania, May 25-26, 2017. Kaunas: LEI, 2017. ISSN 1822-7554, p. V-180 – V-185.

Brief information about the author

Personal data:

Name: **Marius**

Surname: **Urbonavičius**

Date of birht: **February 9, 1988**

Place of birth: **Pagėgiai, Lithuania**

e-mail: marius.urbonavicius@lei.lt

Education:

2006 – 2010	Bachelor’s degree in Applied Physics at Kaunas Technology University
2010 – 2012	Master’s degree in Energy and Environment at Vytautas Magnus University
2013 – 2017	Doctoral studies in Energetics and Power Engineering at Lithuanian Energy Institute

Reziumė

Vandenilio sintezė panaudojant plazmoje aktyvuotų aliuminio miltelių ir vandens reakcijas

Pastangos mažinant šiltnamio reiškinį sukeliančių dujų emisiją ir priklausomumą nuo ribotų iškastinio kuro išteklių skatina naujų, švaresnių alternatyvių energijos šaltinių kūrimą ir plėtrą. Pastaruoju metu vandenilio kuro elementai laikomi perspektyviomis energijos tiekimo sistemomis, galinčiomis prisidėti prie tvarių ateities energijos šaltinių plėtros ir į aplinką išskiriamo CO_2 kiekio mažinimo. Vandenilis pripažintas vienu geriausių energijos nešėjų, kuris sunaudojamas cheminę energiją verčiant elektros energija. Todėl daug dėmesio skiriama ir aplinkos neteršiantiems bei ekonomiškiems vandenilio gavybos būdams.

Šiandieniniame pasaulyje nešiojami elektroniniai prietaisai tapo neatskiriama žmonių gyvenimo dalimi, o prietaisų funkcionalumas sparčiai progresuoja kiekvienais metais. Tačiau naudojamų akumuliatorių technologijos nesivysto taip sparčiai, kaip elektroniniai prietaisai, todėl negali užtikrinti reikiamos galios ilgesniam naudojimo laikui. Iš čia kyla poreikis ieškoti kitokių, efektyvių elektros energijos tiekimą užtikrinančių būdų. Verta paminėti, jog tai ypač svarbu karo pramonėje naudojamų prietaisų ilgaamžiškumui. Dėl didesnio energijos tankio, greito paleidimo ir geresnio efektyvumo PMM kuro elementai gali pagerinti elektronikos prietaisų eksploatavimo charakteristikas. Be to, kuro elementas veiks tol, kol bus tiekiamas vandenilis.

Vandenilio kuro elementai gali būti naudojami tiek stacionariose sistemose, tiek nešiojamuose elektroniniuose prietaisuose. Tačiau, nors vandenilis turi didelę energetinę vertę, o šalutinis reakcijos su deguonimi produktas yra vanduo, praktinį pritaikymą nedidelės galios prietaisuose riboja brangios ir sudėtingos vandenilio gavybos ir saugojimo technologijos. Temos aktualumą parodo rinkoje jau esantys išoriniai kroviklIai (*Horizon MiniPak ir Inteigent Energy Upp*) su integruotais kuro elementais. Be to, kompanija *Apple* taip pat patentavo vandenilio technologijų naudojimą išmaniuosiuose telefonuose ar planšetiniuose kompiuteriuose (*US20150249280*). Tiesa, juose vandenilis saugojamas brangiuose metalų hidriduose.

Todėl minėtos vandenilio saugojimo ir transportavimo sistemos galėtų būti keičiamos į nedideles, vandenilio sintezės pagal poreikį (*in situ*) sistemas, tiekiant vandenilį, išsiskyrusį metalų reakcijos su vandeniu metu. Perspektyvia laikoma *in situ* vandenilio gavyba gali būti pritaikyta mažos galios nešiojamiems prietaisams, turintiems PMM kuro elementus, vykstant aliuminio ir vandens reakcijai. Tačiau Al paviršiuje natūraliomis sąlygomis susidaro vandenyje netirpus barjero sluoksnis, kuris stabdo vandens molekulių patekimą ant metalinės Al dalies.

Atlikus naujausios mokslinės literatūros analizę, buvo aptikta daug informacijos apie skirtingus būdus, skirtus suardyti arba pakeisti barjero sluoksnio struktūrą, ir apie technologinius Al ir vandens reakcijos taikymus elektros energijai generuoti. Nepaisant to, dauguma Al paviršiaus aktyvacijos metodų vadovaujasi brangių arba aplinką teršiančių papildomų medžiagų naudojimu bei labai aukštos temperatūros taikymu, o vandenilio sintezės procesas būna gana lėtas ir neužbaigtas (t. y. sureaguoja ne iki galo). Taigi, reikia kitokių, unikalių sprendimų, norint pašalinti arba pakeisti barjero sluoksnį Al paviršiuje, nenaudojant brangių priemaišų bei su kiek įmanoma mažesnėmis energijos sąnaudomis. Todėl, tuo tikslu, švariomis laikomos plazminės technologijos galėtų būti efektyviai naudojamos paviršiaus struktūrai keisti.

Darbo tikslas – sukurti žematemperatūrės dujų plazmos aktyvacijos technologiją, skirtą aliuminio miltelių paviršiui modifikuoti, ir panaudoti gautas struktūras vandenilio, skirto elektros energijai generuoti, gavyboje iš vandens.

Šiam tikslui pasiekti buvo numatyti tokie uždaviniai:

1. Eksperimentiškai nustatyti optimalius aktyvacijos, skirtos aliuminio milteliams modifikuoti, dujų plazmoje parametrus (keičiant sąveikos laiką, dujų slėgį, išlydžio galią ir atstumą nuo plazmos šaltinio iki bandinio).
2. Ištirti Al miltelių modifikavimo mechanizmą bei nustatyti Al miltelių paviršiaus pokyčių priklausomumą nuo keičiamų aktyvacijos plazmoje parametrų bei sąveikos laiko;
3. Eksperimentiškai nustatyti modifikuotų Al miltelių reakcijos su vandeniu sąlygas, kurioms esant pasiekiamas didžiausias vandenilio sintezės efektyvumas (priedų, vandens kiekio ir temperatūros įtaka);
4. Įvertinti elektros energijos generavimo galimybes, tiekiant Al–vandens reakcijos metu išsiskyrusį vandenilį į protonų mainų membranos vandenilio kuro elementą;
5. Sukurti antrinį γ-Al_2O_3 produktą, skirtą katalizatorių rinkai, iš šalutinio Al–vanduo reakcijos produkto.

Taip pat buvo suformuluoti ginamieji disertacijos teiginiai:

1. Aliuminio milteliai yra efektyviai aktyvuojami bei tokiais išlieka mažiausiai 6 mėnesius po sąveikos su magnetrono generuojama, žematemperatūre vandenilio dujų plazma.
2. Sąveikos su plazma metu hidrofobinis aliuminio miltelių paviršius virsta hidrofiliniu, padidėja polinių molekulių grupių koncentracija bei atsiranda nehomogeniškai pasiskirstę defektai.
3. Plazmoje aktyvuotų aliuminio miltelių ir vandens reakcijos metu išsiskiria beveik 100 % teorinės vandenilio kiekio vertės, o reakcijos kinetiką daugiausiai lemia vandens temperatūra.
4. Vandenilio gavyba, aktyvuoto Al ir vandens reakcijos metu, pagal poreikį gali būti pritaikyta nedidelės galios protonų mainų membranos kuro elementuose, skirtuose elektros energijai generuoti.

5. Neturintis priemaišų nanokristalinis gama aliuminio oksidas, kurio efektyvus paviršiaus plotas >200 m^2/g, gaunamas atkaitinus šalutinį reakcijos – aktyvuotas Al–vanduo – produktą atmosferos oro aplinkoje.

Įgyvendinus uždavinius ir apibendrinus visus atliktus tyrimus, susijusius su aliuminio miltelių aktyvacija plazmoje ir reakcija su vandeniu bei atsižvelgus į iškeltus ginamuosius teiginius, disertacijos darbo pabaigoje buvo suformuluotos pagrindinės išvados:

1. Eksperimentiškai nustatyta, kad efektyvi plazminė aktyvacija galima naudojant magnetroną su Al katodu. Optimaliausi aktyvacijos vandenilio plazmoje parametrai: H_2 dujų slėgis 13 Pa, srovės stipris $I = 1$ A ($P = 250$ W), atstumas x tarp magnetrono ir bandinio 4 cm $\leq x \leq$ 8 cm (esant mažesniam atstumui plazma tampa nestabili), joninės srovės tankis nuo 0,5 iki 1,1 mA/cm^2, aktyvacijos laikas nuo 1 iki 3 valandų. Tokiomis sąlygomis modifikuoti Al milteliai išlieka aktyviais bent 6 mėnesius, laikant juos uždarame inde. Tuo tarpu generuojant plazmą elektrodais, Al miltelių aktyvacija nėra tolygi.
2. Hidrofobinis Al miltelių paviršius virsta hidrofiliniu, nes keičiasi tik paviršiaus struktūra, mažėjant nepolinių molekulių ir didėjant polinių molekulių grupių kiekiui (RSFS analizė). Polinių/nepolinių molekulių grupių santykis padidėjo nuo 0,21 iki 0,45 po plazmos poveikio. Be to, OH grupių kiekio mažėjimas (nuo 58 iki 18 %) ir Al–O ryšiais besibaigiančio paviršiaus susiformavimas taip pat turi teigiamos įtakos Al reaktyvumui vandenyje (RSFS ir dujų analizatorius). SEM buvo stebimi nehomogeniškai pasiskirstę defektai. RSD nefiksavo jokių reikšmingų struktūrinių pokyčių. Taip pat ši technologija gali būti pritaikyta MgH_2 sintezei.
3. Modifikuoti Al milteliai yra pajėgūs generuoti 96 % teorinės vandenilio kiekio vertės (1200 ml ± 2 ml / 1 g Al). Reakcijos su vandeniu efektyvumas ir kinetika gerėja didėjant vandens temperatūrai nuo 25 iki 40 ºC, tačiau esant žemesnei nei 15 °C, reakcija tampa labai pasyvi. Al/H_2O santykis taip pat yra svarbus (0,05g Al + 40 ml H_2O, tai mažiausias vandens kiekis, reikalingas visiškai Al reakcijai per trumpiausią laiką).
4. Al–vanduo reakcija tinkama elektros energijai generuoti naudojant protonų mainų membranos kuro elementą. 1,5 W galios PMM kuro elementas, prie kurio prijungta 2 Ω apkrova, gali generuoti apie 0,7 Wh elektros energijos, naudojant išsiskyrusį vandenilį, visiškai sureagavus 1 g modifikuoto aliuminio 25 °C temperatūros vandenyje.
5. Iš šalutinio reakcijos Al–vanduo produkto atkaitinimo ore metu, 280 °C temperatūroje buvo susintetintas boemitas (AlO(OH)), kurį atkaitinus 500 °C temperatūroje gautas nanokristalinis γ-Al_2O_3 junginys, skirtas

antriniam panaudojimui. Gauto γ-Al_2O_3 efektyvus paviršiaus plotas siekia 247,9 m^2g^{-1}, o kristalitų dydis 5,2 nm. RSD ir RSFS matavimų metu papildomų priemaišų nebuvo rasta, o tai rodo ypač gryno γ-Al_2O_3 sintezę.

UDK 533.9-115+544.41:544.344+661.96](043.3)

SL344. 2018-01-29, 3 leidyb. apsk. l. Tiražas 50 egz.
Išleido Kauno technologijos universitetas, K. Donelaičio g. 73, 44249 Kaunas
Spausdino leidyklos „Technologija“ spaustuvė, Studentų g. 54, 51424 Kaunas