7. Synthesis and research of nanosized materials for hydrogen storage applications

Nanomateriālu sintēze un pētījumi ūdeņraža uzglabāšanas pielietojumiem

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7.1. Review of nanosized materials for energy storage

On November 28, 2018, the European Commission published a strategic long-term vision for a prosperous, modern, competitive and climate neutral economy by 2050 -A Clean Planet for All [1]. The most efficient actions are presented that can lead to achieving net-zero greenhouse gas emissions by 2050 in a cost-efficient manner. The EU, responsible for 10% of global greenhouse gas emissions, is a global leader in the transition towards a net-zero-greenhouse gas emissions economy. The eight scenarios build upon no regret policies such as strong usage of renewable energy and energy efficiency. Most of them look at different technologies and actions, which foster the move towards a netzero greenhouse gas economy. They vary the intensity of application of electrification, hydrogen and e-fuels (i. e. power-to-X), as well as the end user energy efficiency and the role of a circular economy as actions to reduce emissions. In all these pathways electricity consumption increases, but notable differences exist. The pathways that focus predominantly on electrification in end-use sectors see also the need for high deployment of energy storage (6 times today's levels) to deal with variability in the electricity system. To facilitate the transition from fossil fuels to technologies based on clean and renewable resources, problems concerning the energy storage must be solved. Wind and sun are the most popular renewable energy sources, but they are available occasionally or periodically, that is, not at all times required by consumption [2]. Compared to electricity, hydrogen is an ideal energy carrier, because it can be stored almost without losses. In transport sector, hydrogen fuel cell technologies are currently being commercialized (Toyota, Hyundai from 2015), using hydrogen storage in the form of high pressure (700 bar) tanks [3]. The technology and economical means to make carbon composite high pressure tanks capable of providing travel distances up to 700 km – are well understood and the costs are reasonable. International Partnership of Hydrogen Energy (IPHE) [4] has gathered information about an impressive number (>4500) of already realized hydrogen demonstration projects in 9 countries: Australia, Canada, China, Germany, Japan, Korea, New Zealand, Norway, United States of America, and number of active on 2018 hydrogen filling stations (Table 7.1). In the near future, the demand for inexpensive and "green" hydrogen will increase, especially for transportation purposes [1].

Number of active hydrogen filling stations 2018			
State	Number	State	Number
Japan	93	Belgium	3
Germany	44	India	3
USA	39	Netherland	3
South Korea	12	Australia	2
England	11	Finland	2
Denmark	10	Brazil	1
Norway	9	Costa Rica	1
France	9	Czech Republic	1
China	8	Slovenia 1	
Canada	6	Taiwan 1	
Austria	5	Turkey 1	
Italy	4	United Arab Emirates 1	
Scotland	4	Wales 1	
Spain	4		
Sweden	4		
Switzerland	4	Total 2018:	287

Table 7.1. Number of active hydrogen filling stations in 2018 worldwide

Source: The Hydrogen Tools Portal: https://h2tools.org/

High pressure composite vessels can be charged only using powerful multi-stage compressors, which is profitable at filling stations, but not in the private sector and small farms. Creating a capacious, not too heavy and large containers with porous, solid materials containing stored hydrogen could solve this problem, because these materials can be recharged at low pressures, for example, at which typical electrolysers work (up to 30 bar). Regarding the application of this technology for vehicles, the materials with high volumetric and gravimetric densities of hydrogen storage are required [3–5].

Researchers from institutions worldwide are focusing on storage targets defined by DOE [5] of on-board vehicular hydrogen storage systems allowing millage greater than 500 km, while meeting packaging, cost, safety, and performance requirements to be competitive with current vehicles. The respective DOE target for the year 2020 is 4.5 wt% (kg H_2 /kg system) at 233–358 K and 3–100 bars, but ultimate target – 6.5 wt% [5]. Hydrogen safety aspects are important and as it is recognized for transport applications, safest storage method is solid state storage [5, 6]. Different traditional and innovative materials are researched for solid state hydrogen storage, including high surface area adsorbents, metal organic frameworks, and metal hydrides, as well as the approaches that are regenerable off-board such as chemical hydrides and liquid carrier [3, 7].

High surface adsorbents (zeolite and graphene) are the subject of this research. Zeolites as media for hydrogen storage are researched by different authors, and common recognition is that hydrogen adsorbs on zeolite mostly at cryogenic temperatures (below 100 K) [8]. Intercalation of metals in zeolites enhances the amount of adsorbed hydrogen, but no information is found about increase of adsorption temperatures. Different mechanisms are proposed to explain hydrogen binding with zeolites. Xiaoming Du [8] proposes that intercalated cations and oxygen atoms of the framework on pore surfaces are the main adsorption sites of hydrogen molecules at lower temperature, whereas the stable adsorption sites are only oxygen atoms of zeolites framework at higher temperature. Optimum thermodynamic and kinetic windows are needed for hydrogen absorption and desorption in solids at reasonable temperatures and pressures [9]. The pores in zeolites with dimensions of 4 Å -7 Å are suitable to store hydrogen molecules with kinetic diameter of 2.89 Å) up to 1.74% weight fraction, as it is shown, at low temperature (-196 °C) and H₂ pressure (15 bar) [10]. Recently, it was announced that at low temperatures (-196 °C) zeolite templated carbons show an exceptional gravimetric hydrogen uptake - weight fraction 7.3% at 20 bars [11], which is the highest recorded figure for carbon materials. Only some of the research is devoted to hydrogen storage capability in zeolite-type structures at higher temperatures. Weitkamp, et al. in 1993 [12] reported that the zeolites containing sodalite cages in their structure show hydrogen storage capacity 9.2 cm³/g, if loaded at 573 K and at 10.0 MPa.

Carbon nanostructured materials (nanotubes, nanoballs (fullerenes), nanosheets (graphene)) are novel nanoporous materials with ability to become most promising materials for future hydrogen storage [9]. The hydrogen storage in carbon nanomaterials is probably the most controversial topic as far as the solid state hydrogen storage is concerned – the reported gravimetric storage capacity between 10 and 20 wt% was not confirmed [3, 14]. Its storage capacity diminishes to less than 1.0 wt% at the room temperature. Re-adsorption data of Pd, and V-doped CNTs have indicated that more than 70% of hydrogen is spilled onto the low-energy binding sites, such as external wall or groove sites of nanotubes [15]. Transition metal doped CNTs increases the hydrogen adsorption at least by 30%, and it has indicated that more than 70% of hydrogen is spilled onto the low-energy binding sites such as the external wall or groove sites of nanotubes [13, 15]. Studies [16] demonstrate that one can achieve chemical storage of ~5 wt% of hydrogen in few-layer graphene. Using synchrotron spectroscopic techniques and density functional theory DFT calculations, it is shown [17] that only a sub-monolayer amount of hydrogen adsorption on the topmost

layer results in a transition of the entire few-layer graphene (FLG) film from a graphitelike to a diamond-like structure. It was found that the catalytic effect of few-layer, highly wrinkled graphene nanosheet (GNS) addition to MgH_2 reflect on the dehydrogenation/ rehydrogenation performance [18] – lower sorption temperature, faster sorption kinetics, and more stable cycling performance than that of pure-milled MgH_2 .

Carbonaceous materials are attractive candidates for hydrogen storage because of a combination of adsorption ability, a high specific surface area, layered or pore microstructures, and a low mass density. In spite of extensive results available on hydrogen uptake by carbonaceous materials, the actual mechanism of storage still remains a mystery. Hydrogen molecule can interact with carbon surface through van der Waals attractive forces (physical sorption), or dissociate in atoms and are chemisorbed. The physical sorption of hydrogen limits the hydrogen-to-carbon ratio to less than one hydrogen atom per two carbon atoms (i. e., 4.2 wt.%), while in chemisorption, the ratio of two hydrogen atoms per one carbon atom (8.4 wt.%) is reported in the case of polyethylene [17-19]. Physiosorbed hydrogen normally has a binding energy on the order of 0.1 eV, while chemisorbed hydrogen has C-H covalent bonding, with a binding energy of more than 2-3 eV [17]. The graphene has some advantages for hydrogen storage because the sp2 covalent-bonding arrangement of the carbon atoms in the honeycomb structure allows efficient binding to hydrogen atoms [19]. Graphene is stable, light, with high theoretical surface; it is mechanically flexible, and can be charged/discharged in room conditions through hydrogen-carbon binding on local curvatures [19].

As it can be concluded from the above review concerning experimental results only, reversible adsorption of hydrogen on graphene mostly studied at 77 K is not practically applicable and several challenges in practice still remain, such as control of the binding sites, porosities and functionalities. In our work, the natural and synthetic zeolites (clinoptilolite group) as nanoporous material and few-layer graphene layers as nanostructured material are subjects of research for reversible hydrogen adsorption/ desorption. For enhancement of hydrogen storage, the chemical, electrochemical and extraction pyrolysis methods for intercalation of materials are performed with metal and non-metal species (Pd, Li, Mg).

In this chapter our research results have been summarized based on publications [20–22] about the role and properties of nanostructured carbon materials for hydrogen storage applications.

7.2. Methods to synthesize and research nanosized materials

Zeolite is a tetrahedral alumosilicate structure stabilized by various cations. In the case of clinoptilolite, the ratio between Si/Al is > 4, and anionic lattice is supported by Ca, Mg, Na, K cations, which can be exchanged and in natural zeolites vary depending on the site of origin. Our samples of natural Clinoptilolite comes from Ukraine – Sokirnitsa deposit (Ukraine, Transcarpathian region). Zeolite samples were prepared by ion exchange with MgCl₂ (1 mol/l) and washing in deionized water solution. The 1 ml/l salt solutions were prepared to exchange cations in zeolite. For the magnesium, lithium and ammonia ion exchange the washed zeolite samples were placed in 1M salt solutions of MgCl₂, CH₃COOLi and ClH₄N, respectively. The solutes were mixed by magnetic stirring in deionised water for 48 h at 40°C. After the ion exchange procedures, the samples were washed with deionised water at least 3 times and dried in air at 100 °C for 12 h. The zeolite

sample was characterized by XRD and EDS as natural clinoptilolite with some ferrite impurities (Table 7.2).

Element	Series	Norm. at., %	Error, %
Aluminium	K – Series	2.619	0.219
Silicon	K – Series	28.808	1.889
Oxygen	K – Series	65.703	6.984
Potassium	K – Series	1.012	0.108
Sodium	K – Series	0.353	0.066
Iron	K – Series	0.538	0.106
Carbon	K – Series	0.314	0.391
Magnesium	K – Series	0.332	0.059
Calcium	K – Series	0.322	0.060

Table 7.2. Natural Clinoptilolite with Si/Al Ratio 10.319 - EDS results

Doping of natural clinoptilolite with Pd has been done with extraction-pyrolysis method in 1 mol/l PdCl solution, stirring the zeolite sample at 60 °C for 24 h and then heating zeolite at 300 °C while vacuuming sample with fore-vacuum pump. Synthetic zeolite was obtained from precursors in hydro-thermal reactor. XRD and EDS analysis Table 7.3 showed that zeolite with clinoptilolite structure is obtained.

Element	Series	Norm. at., %	Error, %
Oxygen	K – Series	62.038	5.859
Silicon	K – Series	29.635	1.883
Aluminium	K – Series	3.542	0.265
Potassium	K – Series	2.728	0.203
Sodium	K – Series	0.372	0.057
Magnesium	K – Series	0.088	0.033
Carbon	K – Series	1.597	0.345

Table 7.3. Synthesized clinoptilolite sample with Si/Al ratio 8.372 – EDS results

To obtain few-layer graphene (FLG) sheet stacks, the electrochemical exfoliation was used [19], taking graphite industrial waste rod as working electrode. Electrochemical exfoliation of graphene is an alternative to the mechanical or oxidation-driven options for bulk production of graphene from parent graphite [20]. An applied voltage drives the ionic species in an electrolyte to intercalate into the graphite electrode and increase the inter-layer distance. For example, in ammonium sulphate, the sulphate ions and water molecules migrate into the interstitial regions of the graphite and locally form gas bubbles (such as SO_2 , O_2), which forces adjacent sheets apart. We used pulse power supply, pulse sequence 3s : 5s on the working electrode -10 V/+10 V for the synthesis. Piece of graphite

crucible used from bronze metallurgy for recycling it to more useful material. Acidic electrolyte is used to find optimal parameters of exfoliation process (3s : 5s, 1 mol/l H_2SO_4) during which sulphate ions migrate into graphite, and upon the reversal of current graphene sheets are separated from bulk material and reduced during the longer sequence of negatively charged platinum support electrode. Another important step is sample submerging in an ultrasound bath (24 kHz) for 3–24 h. Purification – thinnest sheet material is lightest and can be easy separated with centrifuge or sedimentation. To be sure that the resulting material is graphene, not graphene oxide, the FLG samples were annealed in Ar/H₂ (95 : 5) gas flow 15 ml/min at 600 °C for 4 hours – providing higher degree of reduction. Intercalation with cations was done during exfoliation process, by adding 0.01 mol/l MgCl, Li₂SO₄ solution to 1 mol/l H₂SO₄ solution.

Analysis of material composition, structure and morphology

The initial samples were characterized by X-ray diffraction, SEM (Hitachi S-400N; Bruker D8), elemental composition of samples was determined by EDS analysis. FTIR spectra were obtained with Hyperion 80 experimental device. FTIR spectra were obtained in transmittance mode using chamber consisting of stainless steel and KBr and KSR-5 (Thallium Bromide-Iodide) glasses. Suspended material flakes in ethanol or acetone were evaporated on KSR-5 glass at RT and then vacuumed and heated up to 120–140 degrees using resistance heating near outer glass surface. Then samples were exposed to hydrogen atmosphere at 0.2 bar and allowed to cool down to RT.

Gas sorption measurements

Hydrogen sorption experiments were done by volumetric – Sievert's type method. In sample holder (100 to 475K, 2 bar) attached to RGA-100 Mass spectrometer, to determine exhaust gases of sample and cleanliness of experiment (high vacuum in system and hermetic seal at all times). Registered data have been recalculated to desorption graphs, to show consistency and desorbed hydrogen values. Heating is realized at about 10 deg/min. and only the maximum sorption value is analysed. Our powder samples were tested in non-commercial system which allows to determine process endpoints more precisely than the values during sorption – desorption cycle. Recalculation of pressure difference against mass of sample and weight percent (wt%) of stored hydrogen in solid state are achieved. The second method to calculate amount of hydrogen absorbed in sample was gas analysis using HORIBA EMGA – 830 AC Hydrogen Oxygen Nitrogen gas analyser (experiment limited till 100 s due to sensor saturation). Using this method, the loaded sample was burned in He plasma and compared to hydrogen free samples, which had been degassed. The percentage of gas content was recalculated from the mass of sample.

7.3. Results and discussion of hydrogen absorption peculiarities in nanosized materials

Spectroscopic Raman method is applied to examine synthesized FLG material. Raman Spectroscopy shows, that obtained material, contains various signals at defect ranges, but the number of layers can't be precisely determined if there is not a single layer reference material (Fig. 7.1). In literature, similar Raman spectra [20] suggests that it is few-layered, based on the relationships between 2D and G peaks.



Figure 7.1. Raman spectra- red RLG un MG-FLG samples

SEM images allow to determine layered structure of FLG and result of reduction, layered structures, although present, have decreased in number and more defective surface is visible (Fig. 7.2 (a), (b)). Agglomeration occurs both in reduced and non-reduced samples. In case of graphene multi-layer stacks the reduction is important to increase surface area available for hydrogen adsorption. As it was measured with BET, the non-reduced Mg FLG sample showed significantly smaller surface area. Also, significant trend is clinoptilolite, most likely, it has nanopores, which allow for hydrogen sorption but almost does not show up at nitrogen porosimetry, but for FLG samples, most likely, there are open structures and plate surfaces are the sorption sites. Sievert type volumetric method in temperature region 100–400 K is applied to study an amount of adsorbed/desorbed hydrogen.

For zeolite, SEM images allow to visually interpret the size of particles and pores, although, samples easily polarize – being dielectric, and start moving at high energies of electron beam (Fig. 7.2 (c)).





(b)



Figure 7.2. FLG agglomerate (a), FLG sheet (b) and zeolite (c) after sonification and reduction

Zeolite for hydrogen storage

The partial sorption level of clinoptilolite determined from volumetric measurements was ~1.1–0.6 wt%, also – after hydrogenation, natural clinoptilolite sample had changed color to greyer tone both in Sievert type device and in external hydrogenation apparatus for gas analysis measurements. XRD studies show that zeolite has indeed the heulandite type structure determined by XRF as Clinoptilolite. Gas analyser data showed hydrogen content for natural zeolite from 0.36–0.20 wt% (Table 7.4) [20] depending on the loading method (PCT apparatus or the external hydrogenation) for gas analysis measurements.

Sample	Amount of desorbed Hydrogen, wt%	Temperature of desorption maximum, K	BET surface area m²/g	Pore volume mm ³ /g
Pd Clin	0.32	100	22.65	24.93
Mg FLG reduced	0.36	139	16.90	28.49
Li FLG reduced	0.30	143	16.90	28.49
Pd Clin FLG reduced 2.5%	0.20	100	_	_
Mg FLG	0.05	103	6.91	8.69
FLG reduced	0.04	100	16.25	18.17

Table 7.4. Hydrogen desorption characteristics of measured samples [20]

Few-layer graphene for hydrogen storage

For FLG samples, SEM pictures (Figures 7.2 (a) and (b)) show opened few-layer graphite/graphene structures with a higher surface area than if they were stacked together – determined by BET method – Mg FLG 0.43 m²/g and Reduced FLG – 12.4 m²/g. Calculated thickness from SEM pictures are around 37–54 nm as multilayer material up to 200 nm thickness, containing voids between graphene sheets of couple nm up to several μ m. From the SEM pictures, the structures of graphene/graphite type. It was determined that chemical exfoliation produces open FLG structures. Reducing process breaks up the stacks of material, leaving open structures deep in the particles, but also exposing single sheets of FLG.

Results from hydrogen sorption experiments (Table 7.4) determined that reduced FLG samples do not show capabilities of high hydrogen storage, but cation exchanged graphene shows hydrogen storage capabilities at higher temperatures – this points to necessity to find even more useful intercalation atoms than Li or Mg to make material commercially and practically useful for hydrogen storage.

Active carbon for hydrogen storage

Comparing the hydrogen adsorption performance of activated carbon (AC) from Latvian alder wood with few-layer graphene stacks FLGS intercalated with Li (Fig. 7.3) it can be seen that activated carbon (brown line) starts to adsorb hydrogen at temperature of approx. 230 K.

Calculated value of absorbed hydrogen mass in AC sample approaches 1.3 wt% and is promising value for further research and potential applications. Detailed analysis of the pressure and temperature output data for this sample (Fig. 7.4) shows pronounced hydrogen absorption region (coloured circle) with temperature and pressure oscillations, which indicate an exothermic reaction (heat is released).

If we consider mechanisms such as metal hydride formation, Li should not be favourable as low temperature hydride, but in our system – intercalated graphene surfaces, we are more concerned with stabilisation of defects in FLGS plates, thus Li FLGS is still considered because preliminary results (Fig. 7.4) show small but positive value – 0.1 wt% of adsorbed hydrogen starting from 170 K.



Figure 7.3. Pressure – temperature characteristics of two samples (AC and FLGS+Li) in two different atmospheres – helium and hydrogen. Only cooling curves are shown



Figure 7.4. Pressure and temperature as function of time during cooling and heating sample AC in hydrogen atmosphere

7.4. Conclusions

XRD measurements show that analysed sample of natural zeolite is clinoptilolite with crystalline ferrierite and quartz impurities, but synthesized zeolite is clinoptilolite without impurities. Raman spectra approves the existence of graphene sheets in exfoliated few-layer graphite although wider spectra should be expected for FLG samples.

From volumetric measurements it is determined that the hydrogen uptake in natural zeolite at room temperature is around 0.6–1.1 wt%.

The pyrolytic gas analyser was applied to measure hydrogen amount in exfoliated fewlayer graphite and the values – 0.39–0.46 wt% are obtained. Further studies are needed to intercalate graphene sheets – in few-layer graphite – with metal (Mg, Li, Pd) ions or larger anions to raise the amount of bounded hydrogen at a room temperature. Modified FLG and clinoptilolite show higher desorption values for hydrogen, reaching up to 0.36 wt% at cryogenic temperatures. Non-reduced and non-modified FLG suggests that it is able to realize sorption on defects only at cryogenic temperatures, and this is also true for non-intercalated graphene at low hydrogen pressures. Mg and Li intercalation allows to reach higher temperature and wt% for hydrogen storage in FLG samples. As it is concluded from the results, intercalation of nanoporous zeolite materials is increasing the amount of bounded hydrogen.

Two type mechanisms to bind hydrogen with nanostructured material are proposed – strongly and weakly bonded to material, accordingly next mechanisms: (a) splitting of molecular hydrogen onto catalytic centres (introduced metals) into atomic hydrogen, spillover to specific surface states on substrate material (side defects, dopants); and (b) physical adsorption of molecular hydrogen. Desorption energy is higher for (a) type. Synergy between both adsorption mechanisms could increase amount of adsorbed hydrogen.

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7.6. Kopsavilkums

Rentgendifrakcijas mērījumi rāda, ka darbā analizētie dabiskā ceolīta paraugi ir klinoptilolīts ar kristāliska ferierīta un kvarca piejaukumiem, bet sintezētais ceolīts ir tīrs klinoptilolīts bez piejaukumiem.

Savukārt Ramana spektri pierāda, ka no grafīta eksfoliācijas procesā atdalītās plāksnes ir grafēns, lai gan spektrā būtu sagaidāmas platākas joslas tieši vairāku slāņu grafēnam.

Tilpuma metodē noteikts, ka ūdeņraža daudzums, ko spēj uzņemt dabiskais ceolīts istabas temperatūrā, ir 0,6–1,1 svara % (wt%).

Pirolītiskais gāzu analizators izmantots, lai izmērītu ūdeņradi gāzu sastāvā, kas rodas, hēlija plazmā sadedzinot paraugu. Atrasts, ka ūdeņradis paraugos ir 0.39–0.46 wt% apjomā. Jāturpina pētījumi, modificējot vairākslāņu grafēnu ar metāla (Mg, Li, Pd) joniem vai lielākiem anjoniem, lai palielinātu materiālā saistītā ūdeņraža daudzumu.

Modificētie vairākslāņu grafēna un klinoptilolīta paraugi zemās temperatūrās kā augstāko vērtību uzrāda 0,36 wt% ūdeņraža desorbcijas procesā. Izskatās, ka nereducēts un nemodificēts vairākslāņu grafēns spēj adsorbēt ūdeņradi uz defektainajām vietām tikai kriogēnās temperatūrās, kā arī pie paaugstinātiem spiedieniem. Mg un Li interkalācija vairākslāņu grafēnā ļauj sasniegt lielāku daudzumu adsorbētā ūdeņraža augstākās temperatūrās. Kā var secināt no iegūtajiem rezultātiem, arī ceolītam jonu interkalācija palielina saistītā ūdeņraža daudzumu.

Divi mehānismi tiek piedāvāti, skaidrojot stipri saistīto un vāji saistīto ūdeņradi nanostrukturētā materiālā – (a) ūdeņraža molekulas sašķelšanās un atomāra ūdeņraža pārtecēšana (*spillover*) uz materiāla defektu vietām (slāņu malas, piemaisījumi) un (b) molekulāra ūdeņraža fizikāla adsorbcija materiāla porās, starpplakņu spraugās. Lielāka desorbcijas enerģija nepieciešama, lai atbrīvotu (a) tipa mehānismā saistīto ūdeņradi. Sinerģija starp abiem adsorbcijas mehānismiem var palielināt adsorbētā ūdeņraža daudzumu.