

NANOMATERIALS DESIGN FOR HYBRID HYDROGEN STORAGE IN THE METAL – CARBON SYSTEMS

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Hydrogen is a significant and progressive energy carrier, as energy release can be achieved without producing polluting and harmful by-products, as would be emitted by the combustion of fossil fuels. Hydrogen storage is regarded as one of the most important problems, which have to be solved in the developing area of hydrogen technology and economy, because the common storage systems based on liquefied and pressurized hydrogen exhibit principal drawbacks. According to the technical targets of the US Department of Energy for 2010-2015, the containment parameters of 6-9 wt.% and/or system volumetric capacity of 0.028-0.040 kg/l for hydrogen storage materials should be achieved [1]. Thus, many research projects and programs all over the world are concentrating on the search for hydrogen solid store solutions.

There are two principal mechanisms of hydrogen storage in solids connected with intermolecular forces, which do not cause any change in the electronic patterns (adsorption or physisorption), and interatomic electron exchange, which leads to formation of different hydrogen containing chemical compounds (absorption or chemisorption). Research concentrating on physisorption and chemical absorption systems has largely concluded that physisorption systems cannot achieve the required capacities without maintaining cryogenic temperatures, whereas chemical absorbers store more hydrogen, but have limited kinetics and high desorption temperatures. Recently declared materials design approach is shifting research focus toward the hybrid systems, which could combine capacity of chemisorbing materials with kinetics of physisorption systems.

One of the alternatives of such hybrid (composite) system could be dispersion of nanoparticles of the metals / metal compounds, which chemically interact with hydrogen to form hydrides or other hydrogen containing compounds (amides, imides etc) with high gravimetric/volumetric hydrogen uptake, inside of nanoporous carbonaceous media (matrix) with high specific surface area active for physisorption of molecular hydrogen and provided by the precise porosity / pore size distribution.

For effective physisorption, surfaces suitable for adsorption must be maximized and activated. This may be done by special materials design, as in activated carbons, exfoliated or expanded graphites, carbon nanotubes, carbon pyrolyzed from polymers and some other carbonaceous media including some nanoporous crosslinked or hyper-crosslinked polymers [2-5]. The thermochemical treatments may increase specific BET surface areas up to many thousands of square metres per gram of material. Surface activation may be achieved by ensuring that after rigorous drying is performed, and by gentle oxidation under controlled conditions, leading to the formation and manipulation of porosity. Specific diameter pores may be used to cause pore-condensation, thus providing an energy barrier that must be overcome prior to desorption.

However, current physisorption technology is unable to maintain significant levels of hydrogen uptake at ambient conditions. Thus, the possibility of tuning high capacity chemical sorption materials is being considered. A great number of complex and interstitial hydrides can be formed to store hydrogen, for example LiNH_2 , LiH , $\text{Mg}(\text{NH}_2)_2$, MgH_2 , $\text{Li}_2\text{Mg}(\text{NH})_2$, LiBH_4 , $\text{Al}(\text{BH}_4)_3$, $\text{Mg}_7\text{TiH}_{16}$, Li_3AlH_6 , Mg_2FeH_6 , Mg_2NiH_4 , TiFeH_x , $\text{Zr}_{1-y}\text{NiH}_z$ and some others. Novel works have shown that the particle size of metal and metal-hydrogen alloy clusters, such as palladium, magnesium and various intermetallics such as e.g. LaNi_5 , TiFe [5], determines the reversibility and kinetics of chemical uptake. It is concluded that the small size of the clusters reduces internal levels of stress upon uptake. If the particle size of other sorption systems, such as the high capacity, reversible lithium nitride / imide / amide system, which has been shown to have intermediate phases [6], has a similar effect upon kinetics and conditions required for release, these would offer new possibilities for hydrogen storage solutions.

Thus, nanocomposites prepared on the basis of metal / metal compound – carbon systems can provide application of both principal mechanisms of hydrogen storage in a bulk material. Currently, an emerging phenomenon known as ‘spillover catalysis’ is being investigated. It is suggested the presence of small catalytic particles of metal or

metal compound upon the surface of carbonaceous materials causes dissociation of hydrogen molecules and subsequent sorption of increased amounts of the atomic species [7]. If all these above features could be combined, materials may be created which harness these characteristics together to give rapidly reversible hydrogen storage solutions at near-ambient temperatures.

Besides the combination of the different adsorption-absorption mechanisms, in comparison with other potential hydrogen stores, the systems of metal / metal compound nanoparticles dispersed in nanoporous carbon / partly carbonized matrices also possess several considerable advantages, such as the enhanced stability of nanoscale state of metal and metal compound phases, fast physico-chemical kinetics of hydrogenation / dehydrogenation processes (cycle) and existence of 'functional spaces' in mesoporous structure that is especially important in the case of noticeable increase of absorbent phase volume. The common values of electrical resistance and thermal conductivity, which are inherent to carbonaceous materials, allow to provide their self-heating by conducting electric current directly through a material and simplify the procedures of temperature control.

The potential pathways for preparation of hybrid hydrogen store based on the metal – carbon systems can be selected from a number of manufacturing methods such as:

- impregnation (infiltration) of preliminarily prepared activated carbons;
- impregnation of pre-synthesized crosslinked or hyper-crosslinked polymers with subsequent co-carbonization;
- co-synthesis of "polymeric carbon – hydrogen-active metal compound composition" by applying various polymer and metal-organic precursors.

There are a lot of types of cost-effective activated carbons produced in industrial scale. Most of them are available for impregnation with different solvents containing the precursors of hydrogen chemical absorbents. Although the simplicity of impregnation process is obvious in this case, it is necessary to recognize the lower potential for introduction of considerable amounts of metal / metal compounds into a matrix, which is inherent to this preparative method.

For the similar impregnation process, application of some crosslinked polymers, especially those, which are subjected to swelling in solvents, could be much more successful concerning the potential increase of the maximal amounts of introduced matter. The temperature of co-carbonization for such impregnated polymer

matrices might be reduced considerably, as the value of peak heat-treatment temperature in this case would be limited only by the temperatures of (de)hydrogenation cycle, i.e. chemical formation / decomposition of hydrogen storing compounds. Unfortunately, the method has also certain restrictions in volume ratio between adsorbent and absorbent constituents formed in hybrid store.

The co-synthesis of the precursors for both main constituents of the metal / metal compound – carbon hybrid store, which takes into account all the requirements to the products, possesses a great potential for manufacturing of high-performance materials. However, the absence of methodology for specific co-polymerization and co-carbonization processes, and thus, problems to select the appropriate pathways in a variety of potential organic, metal-organic and polymer syntheses are obvious obstacles to progress in nanomaterials and technology design in the metal – carbon systems for hydrogen storage.

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