

## ESSAY

### Hydrides and Hydrogen Storage

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For the last two centuries mankind has acquired energy from the fossil fuels only. It is only recently that we have realized the drawbacks related with fossil fuel economy such as global warming and contamination of urban air. Many ecological and renewable energy sources have been studied and resulted in development of solar plants and wind turbines among the others. The main issue of the modern energy industry is the lack of capacious energy vessels that is why our circuit operates in the on-demand mode, constantly equalizing the production with the usage. Thus, the renewable energy sources are of limited use because of the non-stable character of wind and sun appearance. Another aspect of the problem is powering of the vehicles which cannot be connected to an external circuit and need the energy container of their own. To answer this problem, the idea of ecologically clean hydrogen economy has emerged. The concept is based on hydrogen – ecologically clean fuel with high energy capacity, which would answer the problem of energy storage.

In order to turn hydrogen into electricity, hydrogen fuel cells have been developed and as a matter of fact they are more than two times as efficient as the normal car gasoline engine [1]. Although this sounds promising, there are still few obstacles to overcome in terms of hydrogen based technology. One of them is the hydrogen storage. There are three major competing technologies for hydrogen storage: high pressure tanks, liquid tanks and solid state metal hydrides. Hydrogen in normal conditions exists in gaseous state of matter and is highly flammable if exposed to air in concentrations greater than 4%. Therefore we have to be aware of safety problems while working with hydrogen. From that point of view high pressure tanks operating at pressures as high as 80 MPa raise safety concerns. That also applies to the liquid cryogenic tanks that operate under temperatures of  $\sim 21\text{ K}$ , which also lose much energy due to thermal losses. Still, high pressure gas tanks reach volumetric density of hydrogen about  $\sim 40\text{ kgH}_2/\text{m}^3$  while liquid cryogenic tanks reach capacity of  $\sim 71\text{ kgH}_2/\text{m}^3$ . Both of these aspects show that solid state hydrides are best candidates for the vehicle storage hydrogen applications because of their safe, low pressure, endothermic process of hydrogen release and capacities reaching 80 – 160  $\text{kgH}_2/\text{m}^3$ . Solid-state tanks operate due to the chemical reaction of absorbing hydrogen into the solid-state crystal lattice of material. The material absorbs hydrogen when exposed to hydrogen under pressure and releases it on-demand when heated. There are two main aspects of solid-state hydrogen storages: the gravimetric capacity of hydrogen and the temperature of hydrogen desorption. Ideal solid-state hydrogen storage would operate in temperature range of  $-40/60^\circ\text{C}$  and would have system gravimetric capacity above 9 wt.%, cycle life-time of 1500 absorption cycles and would be as cheap as  $3\$/\text{kg}/\text{system}$  as stated by US Department of Energy FreedomCAR hydrogen storage system targets for year 2015 [1]. So far, materials studied by scientists meet those requirements separately, but the target material has not been found yet. Therefore, scientists began to study with various materials and improvement techniques such as doping with various catalysts, mixing materials together creating complex composites or alloys and milling them to nano-scale particles.

One group of the promising materials are based on Mg. Magnesium hydride takes form of  $\text{MgH}_2$  and has advantages of being high-capacity (7.6 wt.%), fully-reversible, nontoxic, environmental-friendly and cheap hydrogen storage. However, this material has high dehydration

temperature ( $> 350^{\circ}\text{C}$ ) and poor kinetic properties (absorbs hydrogen very slowly).  $\text{MgH}_2$  on itself is insufficient as a hydrogen storage material. Materials used to store hydrogen are processed into powders. Milling magnesium into nanoparticles has proved to be enhancing its properties in terms of hydrogen absorption and desorption kinetics. This improvement is associated with large effective area of milled nanoparticles. The research showed that reduction of particle and grain size improved both desorption temperature (achieving desorption of 4 wt.%  $\text{H}_2$  at  $\sim 300^{\circ}\text{C}$  [1]) as well as absorption/desorption time [2]. However,  $\text{MgH}_2$  milled to nanoparticles exhibited somewhat lower absorption capacity. Although milling to nanoparticles is beneficial, the material needs further improvement. Therefore, much effort was put to investigate various additives to  $\text{MgH}_2$  which would act as catalysts. One of investigated additive was aluminium, which hydrates into  $\text{AlH}_3$ , exhibits low desorption temperature and suitable hydrogenation/dehydrogenation rate as well as pressure.  $\text{AlH}_3$  forms seven different phases. Three of them:  $\alpha$ ,  $\beta$  and  $\gamma$  decompose at  $\sim 100^{\circ}\text{C}$  and are most desired. Scientists came up with the idea to combine Mg with Al and create an alloy, because the properties of Al in terms of hydrogen storage complement the Mg weaknesses. After studies of such combined alloys, dehydrogenation temperature was reduced (by  $\sim 25^{\circ}\text{C}$ ) although the properties of such alloys are still not practical. Therefore, the next step of research was to add another component to the alloy – transition metal (Ti, Ni, V) in order to further improve the material properties. Transition metals such as Ti, Ni or V act in the alloy as a catalyst, lowering the energy barrier for dehydrogenation of material and improving the reversible process of absorbing the hydrogen. Reported reversible capacities of alloys have values 4.25 wt.% (Ti), 5.58 wt.% (Ni), 5.77 wt.% (V) at  $360^{\circ}\text{C}$  [3]. Another line of investigation is focused on adding complex hydrides to the  $\text{MgH}_2$  such as  $\text{LiAlH}_4$ ,  $\text{NaAlH}_4$  or  $\text{NaBH}_4$  creating complex composite systems. The idea is based on Rule-of-Mixtures (ROM), which states that the desorption temperature of composite system is linear combination of components desorption temperatures and their concentrations. Hydrogen desorption kinetics in those systems is complex and the understanding of different processes occurring in those materials requires more research. Furthermore, some of those additives raise milling problems which again impacts the desorption temperature.

In my opinion the Mg based solid state hydrogen storage materials are promising materials due to many advantages, however the main problem is the high temperature of desorption. The temperature is problematic for hydrogen fuel cells which might be damaged while overheated. Further research of composite systems and alloys of Mg combined with nanostructured milling should yield better material properties. On the other hand, the DOE targets mentioned earlier are too strict in terms with reality. Also the solid state hydrogen storage in my opinion is the most promising technology for hydrogen storage, because the safety argument cannot be overstated.

#### Literature:

- [1]. R. A. Varin, T. Czujko, Z. S. Wronski, "Nanostructured Hydrides for Solid State Hydrogen Storage for Vehicular Applications", Vol. 1 Ch. 6 of the series Progress in Green Energy, pp 223-286, 2011
- [2]. M. Y. Song, Y. J. Kwak, S. H. Lee, H. R. Park, "Comparison of hydrogen storage properties of pure Mg and milled pure Mg", Indian Academy of Sciences, Bull. Mater. Sci., Vol. 37, No. 4, 2014
- [3]. Y. Wang, S. Lu, Z. Zhou, W. Zhou, J. Guo, Z. Lan, "Effect of transition metal on the hydrogen storage properties of Mg–Al alloy", J Mater Sci 52:2392–2399, 2017

## Measured data analysis

Van't Hoff plot based on  $\text{LaNi}_{(5-x)}\text{In}_x$  alloy measured data was made for three stechiometries  $x = 0.1, 0.2, 0.5$  as shown in fig. 1.

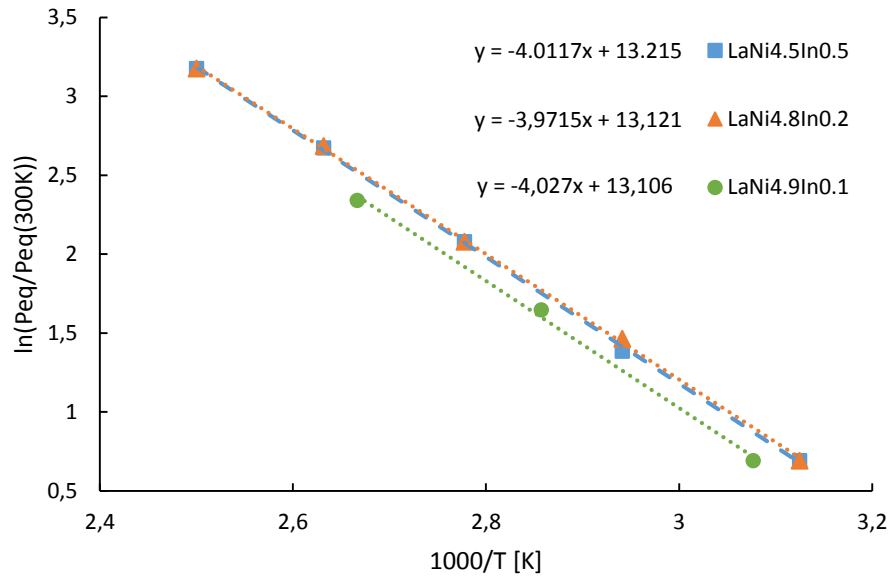


Figure 1. Van't Hoff plot of  $\text{LaNi}_{(5-x)}\text{In}_x$  hydride-forming alloy for three measured stechiometries  $x = 0.1, 0.2, 0.5$ .

Linear function was fitted to each dataset. Hydride formation enthalpy  $\Delta H$  and entropy  $\Delta S$  were then calculated using the linear fit factors. Calculated values are shown in the table 1. below.

Table 1. Calculated hydride formation enthalpy and entropy

x	a	b	$-\Delta H$ [kJ/mol]	$-\Delta S$ [J/mol/K]
0.5	-4.01	13.22	33.35	109.87
0.2	-3.97	13.12	33.02	109.09
0.1	-4.03	13.11	33.48	108.97