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Development of Intermetallic Compounds for Hydrogen Supply System Integrated with PEM Fuel Cell

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Fuel cell power units require high quality hydrogen [1] and problem of their hydrogen supply with the use of intermetallic compounds, which selectively absorb hydrogen from gas mixture and can desorb it at needful parameters, thus excluding hydrogen purification and compression and utilizing waste heat from the fuel cell increasing overall energy efficiency of the power unit.

On the other hand not all the admixtures are safe for intermetallic compounds during hydrogen sorption. The admixtures can be divided into five groups according their influence on sorption capacity and durability of intermetallic compounds [2, 3], Table 1 summarize results for T = 20–100^{o}C and P = 0.001–50 bar. Thus metal hydride hydrogen supply system can purify hydrogen from admixtures of groups 1-3 and requires preliminary purification from oxygen, water and CO (burner and dryer), and sulfur compounds.

Table 1: Influence of admixtures on hydrogen sorption properties of intermetallic compounds.

Group	Admixture	Type of interaction with surface of particles	Number of cycles, N*
1	Ar, He, N_2, CH_4, C_2H_6,…	«Inert»	>1000
2	CO_2, (NH_3),…	Chemisorption without poisoning	~1000
3	C_2H_4, C_2H_2, (C_3H_6),…	Catalytic hydrogenation	~1000
4	O_2, H_2O,…	Chemical reaction	~100
5	CO, SO_2, H_2S, (CH_3SH),...	«Poisoning»	1–2

The following design scheme of metal hydride system can be proposed:

1. Purification system (preliminary purification and metal hydride purification units) – fast operating, compact, easily replaceable high durable intermetallic compound;
2. Metal hydride hydrogen storage unit – thermally coupled with fuel cell, intermetallic compound with high hydrogen capacity.

JIHT RAS experimental setup consist of source of hydrogen, solid-state purification and storage system and 5 kW PEM fuel cell. Water at temperatures from 293 up to 353 K (25 and 80 ^{o}C respectively) is used to control absorption and desorption process. Main advantages of

* Number of hydriding/dehydriding cycles for which hydrogen capacity of storage material decreasing in 2 times for concentration of admixture 0.1% vol.

this scheme are possibility of using of impure hydrogen, simplicity, reliability and safety (Figure 1).

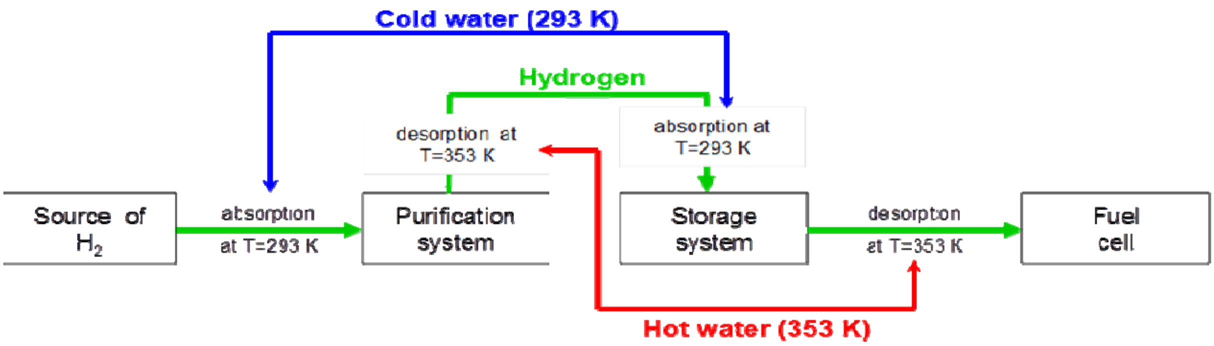

Figure 1: Principle design of 5 kW PEM fuel cell based power unit with solid state purification and storage system.

Two types for hydrogen storage materials are used: purification alloy and storage alloy. Requirements for the purification alloy are: (i) hydrogen absorption pressure must be lower than 1 bar at 293 K to minimize hydrogen losses during purification process; (ii) hydrogen desorption pressure must be as high as possible at 353 K for efficient charging of hydrogen storage unit; (iii) alloy must have good cycle ability. Requirements for the storage alloy are: (i) low absorption pressure at 293 K to make charging easier; (ii) desorption pressure along the whole plateau at 353 K must higher than 6 bar to meet fuel cell power unit requirements for hydrogen supply; (iii) alloy must have good cycle ability.

Alloys compositions was chosen with the use of semi empirical mathematical model, which represents thermodynamic parameters of unknown alloy at hydrogen desorption as a sum of the parameters of the well-investigated alloys with different coefficients [4]. Experimental samples was prepared and investigated by Siverts method and two alloys was chosen [5] for purification and storage units (Table 2).

Table 2: Properties of alloys.

Alloy composition	P_{eq}, bar		Hydrogen storage capacity, % wt.		ΔH_{des}, kJ/mole H_2
	298 K	353 K	298 K	353 K	
Storage alloy $La_{0.5}Nd_{0.5}Al_{0.1}Fe_{0.4}Co_{0.2}Ni_{4.3}$	1.1	11.6	1.1	1	35.3
Purification alloy $LaFe_{0.1}Mn_{0.3}Ni_{4.8}$	0.66	7.6	1.3	1.2	40.4

Purification alloy $LaFe_{0.1}Mn_{0.3}Ni_{4.8}$. was tested on admixture resistance and durability. To model the operation of purification unit a sample of alloy was placed into the autoclave and cycled with impure (nitrogen, oxygen, water) hydrogen at 7 bar and 353 K. Hydrogen storage capacity was measured after each cycle by Siverts method. It is found that absorption of technical hydrogen leads to decreasing of hydrogen capacity down to 20-30% during 25 cycles (Figure 2, left). After 30 absorption/desorption cycles autoclave was set under vacuum conditions and alloy sample was cycled with high purity hydrogen from metal hydride accumulator at 7 bar and 353 K. Hydrogen storage capacity is measured after each cycle (Figure 2, right). There was performed 3 consecutive series of experiments. It is found that making of 7-10 absorption/desorption cycles with high purity hydrogen allows to regenerate hydrogen capacity up to 95% from the initial value.

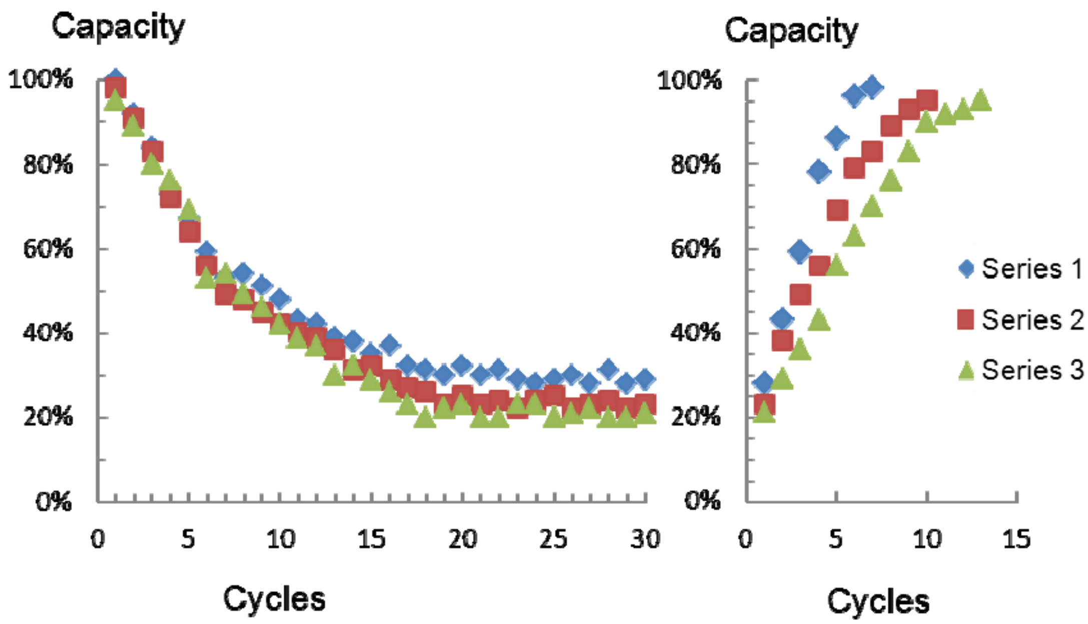

Figure 2: Degradation in impure hydrogen (left) and regeneration in pure hydrogen (right) of 4 g sample of $LaFe_{0.1}Mn_{0.3}Ni_{4.8}$ in three consecutive series of experiments.

It is obvious that multiple regeneration cycles are inconvenient for practical applications, losses of hydrogen and energy will be too high. In this connections experiments with single regeneration cycle were made. An experimental reactor was filled with 489 g of purification alloy $LaFe_{0.1}Mn_{0.3}Ni_{4.8}$. The reactor is a cylindrical vessel with thick steel walls, placed inside liquid bath of thermostat. Between sorption/desorption cycles alloy was poisoned with air from atmosphere. Parameters of experiments are presented in Table 3. Results (Fig. 3) show that dynamics of hydrogen sorption is influenced by air poisoning of alloy but not as great as experiments on smaller sample predict. Also even one cycle of regeneration with pure hydrogen improves the situation.

Table 3: Parameters of experiments on air poisoning of $LaFe_{0.1}Mn_{0.3}Ni_{4.8}$ alloy.

#	Regime	Gas	Thermostat	#	Regime	Gas	Thermostat
1	Sorption	H_2, 7 bar	10°C	4	Sorption	H_2, 7 bar	40°C
	Desorption	to 1 bar	90°C		Desorption	to 1 bar	90°C
	Poisoning	Air for 3 h	90°C		Poisoning	Air for 1 h	40°C
2	Sorption	H_2, 7 bar	10°C	5	Sorption	H_2, 7 bar	40°C
	Desorption	to 1 bar	90°C		Desorption	to 1 bar	90°C
3	Sorption	H_2, 7 bar	10°C	6	Sorption	H_2, 7 bar	40°C
	Desorption	to 1 bar	90°C		Desorption	to 1 bar	90°C

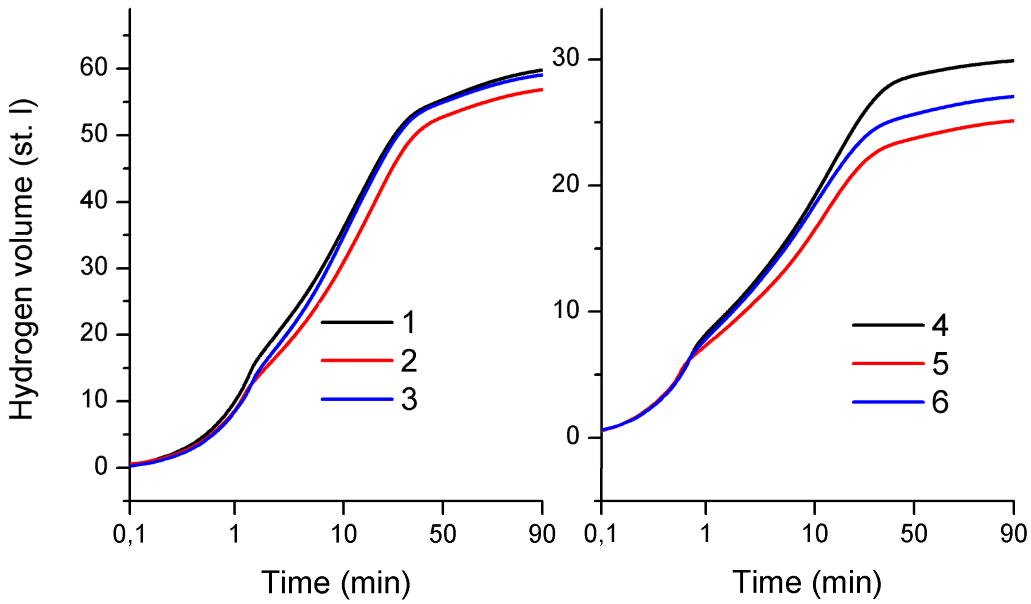

Figure 3: Charged hydrogen for different cycles during experiments on alloy poisoning/regeneration (parameters see in Table 3).

Conclusions

Due to selective absorption of hydrogen intermetallic compounds are good for hydrogen storage and purification in hydrogen supply systems for PEM fuel cells. On the other hand properties of hydrogen storage materials are influenced by impurities in hydrogen and several types of impurities (water, oxygen, sulfur, etc.) can greatly reduce their sorption capacity and durability. It is proposed to use preliminary purification to avoid poisoning of hydrogen storage materials.

For experimental 5 kW PEM fuel cell it is proposed to use the following design of hydrogen supply system:

1. Purification system – fast operating, compact, easily replaceable high durable intermetallic compound. Consists of preliminary purification unit (catalytic burner and dryer) and metal hydride purification unit (LaFe0.1Mn0.3Ni4.8 alloy is chosen);
2. Metal hydride hydrogen storage unit – thermally coupled with fuel cell, intermetallic compound with high hydrogen capacity (for further experiments La0.5Nd0.5Al0.1Fe0.4Co0.2Ni4.3 alloy is chosen).

Experiments on $LaFe_{0.1}Mn_{0.3}Ni_{4.8}$ shows that impurity can greatly reduce quality of the storage material, but it can be regenerated with pure hydrogen. Experiments on reactor scale sample show that even one recharging with pure hydrogen can improve hydrogen sorption rate after air poisoning of alloy.

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