ACTIVATED CARBON AND HYDROGEN ADSORPTION STORAGE

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Introduction

Hydrogen is the ideal alternative for fossil fuel systems. From environmental point of view, it is the cleanest fuel known until recently, and from economic point of view hydrogen technology will be able to revolutionize the transport and energy market.

The objective of this work is to analyze hydrogen storage in several porous carbon materials and its relation with the porous texture, to suggest perspective activated carbon materials. It is devoted to the development of a thermally regulated adsorption storage system for two-fuel (hydrogen and natural gas) automobile with the engine of internal combustion.

Results and discussion

Activated carbon fibers "Busofit" and granular activated carbons (additionally activated by us and commercially available) have been used in this work**.** According to the offered technology samples from "Busofit" have been prepared by selective thermal processing at high temperature 850 °C in an gas atmosphere. Wood-based carbons (5–7) were produced by controlled pyrolysis of waste wood and special activation [1]. The atmosphere of carbonic gas appeared more preferably oxygen for growth of a specific surface and sorption capacity.

The N_2 and H_2 sorption isotherms were measured with the High Speed Gas Sorption Analyser NOVA 1200 at 77 K in the pressure range 0 – 0.1 MPa. Table 1 summarizes the results of the physisorption measurements of the materials analyzed. All samples are highly micro-and mesoporous carbon materials. As seen in Table 1, the greatest values of a surface area and micropore volume among carbon fibrous materials has "Busofit-M8"; from wood-based activated carbons it is stand out "WAC 3-00", from granular carbons – "Sutcliff". They are also the best stores of hydrogen (accordingly 253, 221 and 237 ml(STP)/g) due to physisorption.

Table 1. Textural characteristics and hydrogen-sorption capacities at 77 K and 0.1 MPa for the researched carbon materials

No	Sorbent	a_v, ml/g	a, wt%	S_H, m^2/g	S_{BET}, m^2/g	S_{DR}, m^2/g	V_{DR}, ml/g	V_t, ml/g	R_{DR}, Á
1	Busofit 191-5	199.9	1.76	462	1691	2496	0.887	0.234	49.9
2	Busofit-M2	203.9	1.79	465	1702	2507	0.89	0.43	41.5
3	Busofit-M4	225.1	1.98	536	1715	2547	0.9	0.42	42
4	**Busofit-M8**	**252.9**	**2.23**	**571**	**1939**	**2985**	**1.04**	**0.27**	**51**
5	WAC 97-03	115	1.01	271	715	1050	0.37	0.33	33.4
6	WAC 19-99	172.1	1.51	393	1005	1486	0.53	0.44	41.7
7	**WAC 3-00**	**221.1**	**1.95**	**575**	**1383**	**2142**	**0.74**	**0.22**	**50**
8	207C	209.2	1.84	502	1300	1944	0.69	0.37	41
9	Norit sorbonorit-3	193.8	1.71	458	1361	2044	0.73	0.26	50
10	Sutclife	236.6	2.08	527	1925	2864	1.02	0.254	53.6

Note: WAC – wood-based active carbon; a_v – volume capacity of hydrogen storage using physisorption, a – capacity of hydrogen storage using physisorption, S_H – BET surface area determined on hydrogen; S_{BET} – BET surface area determined on nitrogen; S_{DR} – surface area, determined on Dubinin-Radushkevich method, V_{DR}– micropore volume, determined on Dubinin-Radushkevich method, V_t – mesopore volume, determined on t-method, R_{DR} – size of pore, determined on Dubinin-Radushkevich method, Á.

The approach of research institutes AGLARG group [2] was used for an operative estimation of gas sorption capacity for carbon sorbents. According to it micropore volume and the specific surface area have been choose as determining parameters. For reception of the function approximating dependence of hydrogen sorption capacity on carbon materials from value of a specific surface area (at pressure 0.1 MPa and temperature 77 K), we used the own experimental data (Table 1) and an experimental database [3].

For carbon samples we have found linear relationship between BET surface area and volume

sorption capacity of hydrogen at 77 K and 0.1 MPa as:

$$a_v = 0.0783\, S_{BET} + 84.02 \qquad (1)$$

Influence of micropore volume on sorption capacity of hydrogen for various carbon materials under the chosen conditions (77 K, 0.1 MPa) is well described by the following linear correlation:

$$a_v = 119.12 V_{DR} + 115.41 \qquad (2)$$

There is a general need to have a good fit of experimental isotherms and temperature and to extrapolate some isotherms beside the experimental field. Physisorption on microporous carbons can be described with the Dubinin-Radushkevich equation

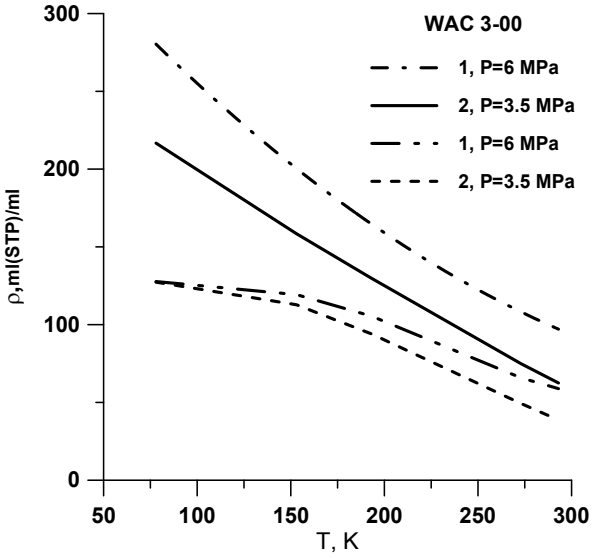
$$a_{eq} = \frac{W_0}{v_a} \exp\left\{ -\left[\frac{R_\mu T \ln\left(P_{sat}/P\right)}{E} \right]^2 \right\}. \qquad (3)$$

where $P_{sat} = P_{cr}(T/T_{cr})^2$ (4)

As a results of the experiments, we obtained hydrogen sorption isotherms for different carbon materials and empirical coefficients for the Dubinin-Radushkevich equation (3).

The mathematical model of hydrogen adsorption storage cylinder based on the system of equations: energy balance, kinetics and equilibrium state (the equation of an isothermal adsorption). The kernel of the problem is the non-stationary heat-balance equation with the source item, which takes into account the heat of sorption and the presence of the heat exchange element (heat pipe). The heat pipe allows us to use different sources of energy and to control a temperature distribution in a sorbent bed, to regulate a degree of gas output and a time of storage discharge. The suggested simple model gives us a possibility to obtain the field of temperature and gas concentrations during charge-discharge procedure of the gas cylinder.

A set of calculations was performed in the interval of the ambient temperatures from 78 to 273 K. The high-surface area activated carbon fiber "Busofit-M8" and wood-based carbon "WAC 3-00" were chosen as promising gas sorption materials to design a hydrogen storage system. Figure 1 shows the plot of the volume storage density of hydrogen in the cylinder with allowance for a compressed gas (1) and without allowance for it (2, the adsorbed phase) as a function of ambient temperature.



Resume

To improve the parameters of the hydrogen storage system the activated carbon fiber "Busofit" and wood-based carbon were suggested. Some sorption capacity ant textural data for new materials were obtained. Optimization of sorbent and sorption conditions is expected to lead to storage capacity of 500–600 ml(STP)/g, close to targets set for mobile applications.

The employment in gas accumulator of a heat-monitoring device on the heat pipes enables one to control the temperature of sorbent bed and provide optimum operational conditions.

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References

1. Vasiliev LL, Kulakov AG, Mishkinis DA, Safonova AM, Luneva NK. Activated Carbon For Gas Adsorption. III Int. Symposium Fullerene and Semifullerene; Structures in the Condensed Media, 22-25 June 2004, Minsk, Belarus:110–115.

2. Adsorbed Natural Gas Research Conducted by Atlanta Gas Light Adsorbent Group (AGLARG). Final report 1990-1993 Gas Research Institute, Atlanta GRI-95/0068, 1994.

3. Nijkamp MG, Raaymakers JEMJ, Dillen AJ, Jong KP. Hydrogen storage using physisorption – materials demands. Applied Physics A. Materials Science & Processing 2001. A72:619–623.