Experimental investigations of adsorption characteristics and porosity of activated metal hydride powders

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Abstract. In the present work non-uniformities of microstructure, porosity and adsorption characteristics of La0.9Ce0.1Ni5 metal hydride by the height of the bed are investigated. A 500 g metal hydride bed was cycled inside a vertical metal hydride reactor and three samples was taken from top, middle and bottom of the bed. Non-uniform particle distributions and bed densification were observed, the bed porosity is around 0.58-0.67 at the top and middle parts of the bed and 0.46-0.54 at the bottom, where a dense and robust agglomerate was formed during the cycling. Specific surface area measured by nitrogen adsorption methods is 1.8-2.1 m$^2$/g at the top of the bed, 4.2-5.4 m$^2$/g in the middle and 1.1-1.5 m$^2$/g at the bottom. The maximum is connected with higher degree of particle dispersion without effects from particle agglomeration.

1. Introduction

Growth of environmental crises such as emission of greenhouse gases, environmental pollution by fossil fuels, have attracted attentions to substitute the gasoline by renewable and green energy solutions. However, most renewable energy sources cannot supply a steady source of electrical energy, thus electricity storage method is required. Hydrogen is a perspective candidate as a secondary energy carrier for electrical energy storage from renewable sources due to high specific heat of combustion and environmental friendliness [1].

Main obstacle of wide application of hydrogen is its storage process. Metal hydrides (MH) are promising materials for safe methods of hydrogen storage because they do not easily explode. The solid-state metal hydride material has advantages in comparison with the conventional compressed gaseous or liquid H$_2$ storage: high volumetric density, high H$_2$ absorption capacity, moderate working temperatures and charging pressures for H$_2$ storage; all these make the metal hydrides a considerable choice [2].

Along with the pressure-composition-temperature (PCT) diagram of metal hydrides, a heat and mass transfer in a MH powder bed is another key parameter for practical application of metal hydride devices. Metal hydrides are used in a powder form with average particle size of 1-10 µm to increase the reactive area. The limiting heat transfer property of the powder is an effective thermal conductivity (ETC) of the entire packed bed, which is quite low (around 0.1-1 W/m K). The ETC depends primarily on a hydrogen pressure, while a temperature has only an indirect influence [3], also porosity and packing of a bed are significant for determination of the ETC [4]. Different methods to enhance heat transfer rate on MH reactors exist, including internal or external heat exchangers [5], insertion of Ni or Al foam [6], compaction of metal hydride powder with expanded graphite [7], etc.

Generally, the porosity is assumed to be 0.5 and to remain unchanged by sorption/desorption processes, and the assumption is not true in practice. Experimental investigations [8] report porosity values in the range from 0.61 to 0.67. Also porosity can be affected by granular segmentation, densification and growth...
of agglomerates inside the bed. Saito et al. [9] observed a sudden step of strain during cycling and conclude that packing density over 0.4 with rare earth series metal hydride creates a danger of reactor rupture. Nasako et al. [10] define the internal stress accumulation as a two-step process of initial agglomeration between the hydride particles for packing fractions is higher than 61 vol% and the following increase of packing fraction at the vessel bottom as the fine powder generated by pulverization falls down. Mellouli et al. [11] conclude that the expansion and contraction behavior of powder bed has been very little studied in the context of the effects on the heat and mass transfer through the medium, thus experiments are needed to obtain data on metal hydride bed structure.

The objective of this work is experimental investigations of tree samples taken from an activated and cycled La₀.₉Ce₀.₁Ni₅ metal hydride bed from a vertical tubular reactor in order to determine porosity of the bed adsorption characteristics of surface of IMC particles.

2. Experimental details
An intermetallic compound (IMC) La₀.₉Ce₀.₁Ni₅ prepared by arc melting, ingots were crushed manually into 2 mm particles and a sample of weight 500.517 g was placed into the vertical tubular reactor of 180 mm height and 45 mm diameter, and the sample fills about a half of the inner space of the reactor. The sample activated and cycled in US-150 test facility [12]. Activation procedure includes 10 cycles of hydrogen absorption at 9 MPa and 373 K and desorption during 8 hours each cycle. Then the bed was used for cyclical hydrogenation/dehydrogenation for PCT measurements in horizontal and vertical orientations of the reactor [13].

After the cycling, the metal hydride reactor was fully evac uated to residual pressure 10⁻⁵ Pa at 373 K, cooled down, filled by inert gas to avoid ignition of the activated powder, and then opened to the air. Three samples at different heights (10 mm, 45 mm and 80 mm of the bottom of the reactor) were taken for further investigation.

Investigations by means of standard contact porosimetry is conducted by porosimeter Porotech 3.1 (Canada) The data are obtained at 318 K from a tablet form sample of unpressed powder coated with a thin non-woven membrane of polysulfone. Impregnation of the samples is carried out for 1 h in deionized water (specific resistance 16 MΩ·cm at the temperature of 293 K and the pressure of 75 kPa. The drying time for each sample is 2 hours at the temperature of 443 K and the pressure of 75 kPa.

In addition, adsorption characteristics of the samples were analyzed by nitrogen adsorption/desorption experiments, which were conducted at 77 K using Quantochrome Nova 1200 gas sorption analyzer (Quantochrome Instruments, USA). The specific surface area of the samples was calculated from the N₂ adsorption data, at relative pressures between 0.05 and 0.35, by employing the Brunauer-Emmett-Teller (BET) multi-point method and Dubinin-Raduschkevich method.

3. Experimental results and conclusions
The metal hydride bed after the cycling appeared to be highly inhomogeneous. SEM images of the samples and results obtained by standard contact porosimetry are presented in figure 1 and table 1. The bed near the bottom is a dense and robust agglomerate of small and huge particles, in the middle and at the top the particle distributions are more uniform. The pore size in the entire volume of the metal hydride bed is in the range of 100-400 nm with mean size about 250 nm, which indicates the high homogeneity of the La₀.₉Ce₀.₁Ni₅ powder. Porosity decreases from the top to the bottom, which is connected with densification (3.26 g/cm³@80mm, 3.47 g/cm³@45mm, 3.86 g/cm³@10mm, while XRD density of IMC is 8.31 g/cm³) of the bed during the cycling with formation of agglomerates. Values of porosity calculated from the fill density 0.61@80mm, 0.58@45mm, 0.54@10mm differ from the values obtained by the contact porosimetry method (0.67@80mm, 0.63@45mm, 0.46@10mm). Since the Porotech 3.1 operated at the lower limit of measurement, the results calculated from density seem to be more reliable. The values of porosities for the top and the middle of the bed are very close to those measured and calculated by Matsushita et al [8], at the bottom the stress caused by the bed “breathing” leads to particle agglomeration to more dense packing.
Figure 1. SEM images and pore size distributions for the three samples.

Table 1. Porosity and specific surface area for the La$_{0.9}$Ce$_{0.1}$Ni$_5$ bed.

| Parameter                                      | @80 mm | @45 mm | @10 mm |
|------------------------------------------------|--------|--------|--------|
| Fill density (Quantochrome Nova 1200), g/cm$^3$| 3.26   | 3.47   | 3.86   |
| Porosity (from density)                        | 0.61   | 0.58   | 0.54   |
| Porosity (contact porosimetry Porotech 3.1)    | 0.67   | 0.63   | 0.46   |
| Specific pore volume (Porotech 3.1), cm$^3$/g  | 0.206  | 0.182  | 0.119  |
| Specific surface area (Multi-BET), m$^2$/g     | 1.8    | 4.2    | 1.1    |
| Specific surface area (Dubinin-Raduschkevich), m$^2$/g| 2.1    | 5.4    | 1.5    |
| N$_2$ adsorption energy (Dubinin-Raduschkevich), kJ/mol | 2.19  | 1.92  | 1.95  |

Calculation of adsorption methods using Quantochrome was carried out by approximating the linear sections of adsorption isotherms in the applicability ranges of the methods. The correlation coefficient for all methods $R^2 \geq 0.99$. Adsorption isotherms for the BET and Dubinin-Raduschkevich methods are presented in figure 2. $P$ and $P_0$ are the equilibrium and the saturation pressure of adsorbate, $W$ is the adsorbed gas quantity. The isotherms follow the BET model very well, with linear segments from $P/P_0 = 0.05$ to 0.35, on the other hand they do not fit to the Dubinin-Raduschkevich model. Thus, we can conclude that the adsorption process is not a volume filling in micropores, but mono- or multilayer adsorption on the surface of particles in macropores (>50 nm).

There is an evident maximum of the specific surface value in the middle of the bed. This can be explained by two factors. Firstly, granular separation in metal hydride beds during cycling causes smaller particles to move down and concentrate in lower parts of metal hydride devices. SEM images in figure 1 illustrate this. Thus, specific surface should grow from the top to the bottom of the bed [10]. Secondly, stress accumulation near the bottom of the bed leads to densification and agglomerate formation and prevents destruction of big particles, resulting in decrease of the specific surface value. The aggregate formation tends to occur easily due to the increase of cohesion and friction in the metal hydride powder during cycling [9]. Experiments [14] show that the agglomeration regions had a packing ratio of about 0.6 and more, and hydrogen packing causes agglomeration regions to form over a wider area.
Figure 2. Adsorption curves for BET (a) and Dubinin-Radushkevich (b) methods.

The performance of metal hydride reactors is strongly influenced by heat and mass transfer and thermo-physical properties of the bed [15] and variation of porosity can significantly change bed permeability [16] and effective thermal conductivity [4]. Melloulil et al. [11] argue that in their calculations heat and mass transfer processes were not considerably affected by the deformable behavior, but they used a quite simple linear model for the effective thermal conductivity, which does not include dependence of gas thermal conductivity on Smoluchowski effect [17].

We can conclude that non-uniform particle distributions are features of hydrogenation/dehydrogenation cycles, and non-uniformities inside metal hydride have direct influence on complex processes of heat and mass transfer in porous media during chemical reaction of hydrogen adsorption/desorption. Intensification of the heat and mass transfer can be reached by concentration of energy fluxes at small temporal and special scales, by creation of external influence with the aid of “geometrical” non-uniformities in a form of developing of heat exchange surfaces and composite structures and by action of external fields, even electric fields. Understanding of the mechanisms of influence on processes from a surface of a single particle up to collective processes at a reactor scale will open a way to intensification of heat and mass transfer due to decreasing of an activation energy, active manipulation of pressure-concentration-temperature phase diagram and increasing of effective thermal conductivity.

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