HYDROGEN STORAGE IN WELL- SIZED POROUS CARBONS PREPARED FROM SILICA TEMPLATES

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Introduction

It is widely assumed that the critical factor for implementing fuel cells as an energy supply is efficient, cheap, safe and reversible hydrogen storage. Taking into account the law volumetric and gravimetric density of hydrogen, several methods have been considered to achieve this goal [1]. Among them, hydrogen storage in a solid matrix, especially in carbon materials seems to be one of the most promising [2]. A large variety of nanostructured and active carbons has been studied using either gas adsorption or electrochemical decomposition of water [3,4]. A significant effort has been undertaken to depict ideal carbon structures for hydrogen storage. Unfortunately, for most of the commercially available carbon adsorbents a strict control of the pore size is precluded. Therefore, the possibility to synthesize nanostructured carbons with a well-defined texture by a templating procedure is of great interest [5-9]. In this study, these materials are investigated as reversible hydrogen storage medium. The hydrogen uptake is correlated with the microtextural characteristics of the nanostructured carbons.

Experimental

Two kinds of silica templates, MCM48 and SBA-15 were used as a host for the preparation of the nanostructured carbons. Detailed information about the synthesis of the silica templates is given in references [5-6]. The pores of the templates are filled using two routes: chemical vapour infiltration (CVI) from propylene, liquid impregnation with a sucrose solution or pitch followed by carbonization [7-9]. Carbon materials with an ordered porosity are obtained after removal of the silica template by HF treatment. They display an interconnected three-dimensional porosity constituted of micro-and mesopores. The nanostructured carbons synthesized from the MCM48 or SBA15 mesoporous matrix are named in the text CXY (C for carbon; X = Pr, S or P for propylene, sucrose or pitch, respectively; Y= 48 or 15 for the templates MCM-48 or SBA-15, respectively). The pore texture of the carbon materials has been studied by nitrogen adsorption at 77 K, and CO_2 adsorption at 273K. It seems that the pores which could be occupied by hydrogen are better estimated taking into account $V(CO_2)$ determined by the Dubinin Radushkevich equation [10].

The hydrogen storage ability is estimated in a three electrode cell by galvanostatic electrodecomposition of a 6 mol.L^{-1} KOH aqueous solution and voltammetry experiments, using nickel as a counter electrode and Hg/HgO as a reference electrode (0.098 V vs. NHE). The hydrogen uptake is evaluated from the faradaic charge consumed for the hydrogen oxidation process. The experiments were set in a wide range of electric regimes. The mass of the active material in the working electrode is ranging between 10-13 mg in the dried state. The electrodes are in the form of pellets prepared by pressing a homogenous mixture of the examined carbon material (85wt %), acetylene black (5wt%) and polyvinylidene fluoride - PVDF-Kynar Flex 2801 Atochem (10wt %). The electrochemical measurements were performed using a VMP potentiostat/galvanostat (Biologic, France).

Results and Discussion

The mesoporous silica material named MCM48 is characterized by a cubic structure built by two interlacing networks of channels. The material referred as SBA-15 is described as 1-D hexagonal rods giving cylindrical pores. Smaller pores are located perpendicular to the 1-D channels. The selected templates demonstrate a highly organized porous structure and a narrow pore size distribution [5-6].

Various electrochemical behaviours are observed for the nanostructured carbons, depending on the carbon precursors and infiltration process. The galvanostatic charge/discharge characteristics of the highly ordered carbons are presented in Figure 1. In order to estimate the maximum storage ability, a 500 mA/g charging current density is applied for 12 hours. Due to such extreme charging conditions, the high overvoltage allows hydrogen penetration in the micropores to be forced [3]. Once charging is performed, and after 1 hour relaxation time, a moderate oxidation current is applied (25 mA/g). In order to evaluate the amount of energy reversibly stored, the potential of the charged electrode after relaxation is chosen as the beginning of the discharge process and we assume that the complete discharge is reached when the initial open circuit voltage is reached. However, the voltammetry data show that there is still hydrogen remaining in the carbon materials even when the discharging voltage reaches 0.1 V vs. NHE. The energy storage ability of the selected materials is presented in table 1 and compared with their microtextural data.

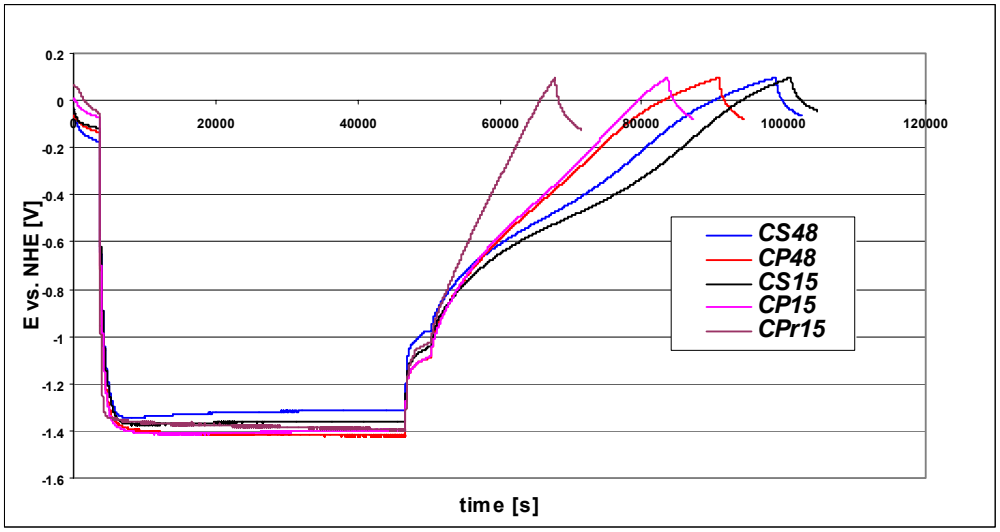

Figure 1. Galvanostatic charge/discharge characteristics of the well-sized mesoporous carbons. Charging current 500 mA/g. Discharging current 25 mA/g.

Sample	Carbon precursor	Template type	TSA [m^2/g]	V_{CO_2} [cm^3/g]	Energy stored [mAh/g]	Capacity [F/g]	Hydrogen stored [mAh/g]
CPr15	CVD	SBA15	713	0.1	120	73	100
CP48	Pitch	MCM48	800	0.18	281	125	246
CP15	Pitch	SBA15	750	0.19	228	120	195
CS48	Sucrose	MCM48	1400	0.36	350	160	306
CS15	Sucrose	SBA15	1300	0.27	350	140	311

Table 1. Energy storage ability and porous texture of the carbons examined by galvanostatic charge/discharge. TSA: total surface area measured by N_2 adsorption, V(CO_2): Micropore volume measured by CO_2 adsorption.

As expected the highest values of the total energy reversibly stored are obtained for the templated carbons with the most developed microporosity. The samples synthesized with the use of the sucrose solution as carbon source give values up to 350 mAh/g. Although these carbons recover the mesoporous character provided by the silica template, they present a well developed microporosity due to their autoactivation during sucrose carbonisation [11]. However, not all the restored energy can be ascribed to the oxidation of adsorbed hydrogen. The ordered mesoporous carbons were already reported as excellent candidates for supercapacitor electrodes [11]. Therefore, the contribution of the double layer capacitance was evaluated from the voltammetry data (table1), and subtracted from the total energy recovered (taking a voltage range of 1V), that gives the real hydrogen uptake. Quite a proportional dependence between the amount of hydrogen reversibly stored and V_{CO2} is observed, that confirms that hydrogen adsorption is strongly related with the presence of small micropores.

The effect of overvoltage was studied for two charge limits (300, 450 mAh/g) using three charging current densities (25, 30, 50 mA/g), and the charge output was measured (table 2). For both charge limits, the energy restored increases with the value of charging current. It confirms that stronger the electric current applied, lower (more negative) the voltage reached during the charging process and higher the polarization giving the necessary energy to force hydrogen to penetrate in the micropores.

Charging current [mA/g]	Charge limit [mAh/g]	Charge output [mAh/g]
25	300	150
30	300	170
50	300	180
25	450	200
30	450	210
50	450	225

Table 2. Energy storage ability of the sucrose based carbon CS 15 for different charging currents.

Taking into account that upon application of a high current the system is far from the thermodynamic reversibility, an equilibrium curve has been obtained by setting a periodic relaxation of the examined cell during the galvanostatic charge/discharge (figure 2). A current of 25 mA/g is applied for one hour, then the

system is allowed to relax for 2 hours, and so on. This experiment allows the reaction close to the equilibrium to be observed, as well as the effect of overvoltage on the amount of hydrogen stored to be checked. The vertical sections visible on the plot represent the voltage change between the beginning and the end of each relaxation period. This difference corresponds to the overall polarization of the carbon electrode (overvoltage) which depends mainly on the system resistance, relatively slow transport processes and electrochemical reactions. At the beginning of both charging and discharging processes the polarization is not very high, being affected by the ohmic drop. The increase of polarization with time is caused mainly by a limited transport (diffusion).

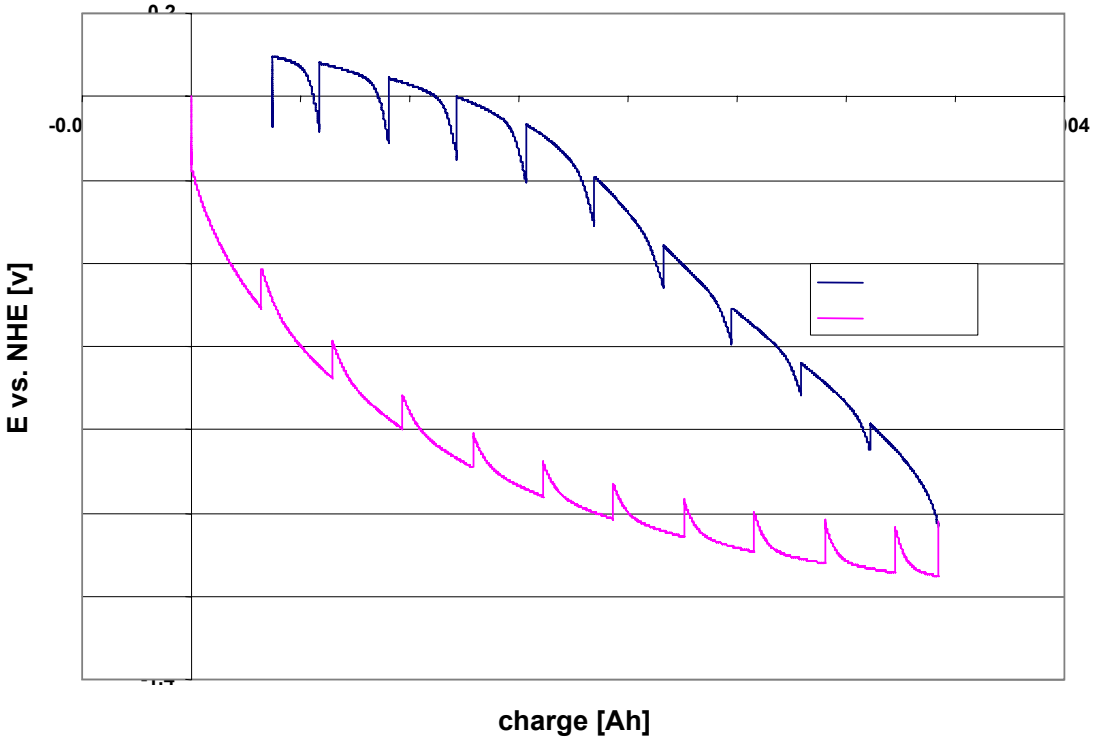

Figure 2. Galvanostatic charge/discharge of the carbon CS15 with a periodic relaxation. Charging/discharging current: 25 mA/g. Potential limit: 1.15 V vs. NHE. Electrolyte: 6M KOH

As an additional examination of the reversible reduction of an aqueous alkaline solution, voltammetry experiments in 6 mol.L^{-1} KOH were performed at a constant scan rate of potential (5 mV/s), extending the potential limits with the cycle number (Figure 3). A systematic widening of the negative voltage limit allows determining the exact potential where the adsorption takes place. On the other hand, the data recorded with the narrow potential window describe the pure capacitance behaviour.

In the case of samples with a developed microporosity, a perspicuous anodic response is visible when the potential of electrolyte decomposition is reached (figure 3). A significant hump appears in the cycle no. 5 and becomes more distinct with the increase of cycle number being located at –0.4 vs. NHE for the last cycle. It is another proof that the overvoltage is a critical factor for hydrogen uptake. A shift of this reaction peak was already reported for microporous active carbon [12]. The peak

shift phenomena can be correlated with the oxidation of hydrogen packed in adsorption sites with high attraction energy. It proves that the hydrogen oxidation proceeds until 0.1 V vs. NHE without carbon overoxidation.

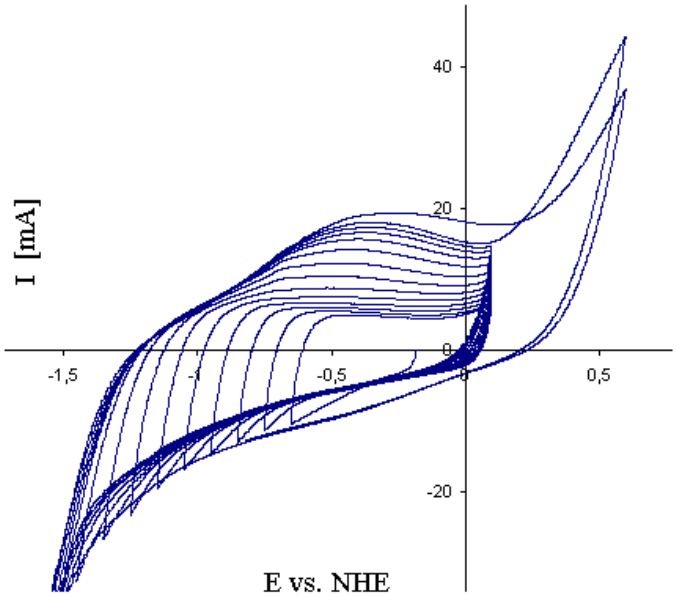

Figure 3. Voltammetry characteristics of the material referred CP48 at a scan rate of 5 mV/s.

Conclusion

It is clear that the carbons prepared by sucrose impregnation exhibit the best energy storage ability among the selected set of samples. The presence of a well balanced micro- mesoporosity appears to be the main parameter which controls hydrogen adsorption. Especially, it seems that small micropores, as those determined by CO_2 adsorption, are quite adapted for trapping hydrogen. Further work should better investigate the optimal pore size in the region of small micropores.

The hypothesis about the crucial role of the overvoltage reported previously was confirmed. The voltammetry data as well as the analysis of the relaxation curve confirm the presence of adsorption sites with a strong bonding character.

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