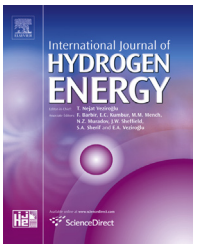
INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2014) 1–11

Available online at www.sciencedirect.com

ScienceDirect

journal homepage: www.elsevier.com/locate/he



Critical findings during the optimisation of hydrogen storage in vapour grown carbon fibres

David Martín y Marero [a,b,c,*], Antonio Madroñero [d]

[a] Departamento de Física Aplicada, Facultad de Ciencias, Universidad Autónoma de Madrid, 28049 Madrid, Spain
[b] Fundación Parque Científico de Madrid, Campus de Cantoblanco, 28049 Madrid, Spain
[c] Centro de Microanálisis de Materiales & Instituto Nicolás Cabrera, Universidad Autónoma de Madrid, 28049 Madrid, Spain
[d] Centro Nacional de Investigaciones Metalúrgicas, Consejo Superior de Investigaciones Científicas, 28040 Madrid, Spain

ARTICLE INFO

Article history:
Received 1 April 2014
Received in revised form
5 June 2014
Accepted 9 June 2014
Available online xxx

Keywords:
Hydrogen storage
Vapour grown carbon fibres
Ion beam analysis
Annealing treatment
KOH activation
Electrolysis

ABSTRACT

The storage of hydrogen in vapour grown carbon fibres samples, according to different well known manufacturing processes, is studied. The main differences between the samples are: the precursor gases composition; the application of an annealing treatment in different atmospheres; charging by absorption in a high pressure hydrogen atmosphere; and finally, chemical and electrochemical treatments. The techniques used for the fibres characterization were: Rutherford backscattering and elastic recoil detection analysis with 2 MeV He^+ ions.

The study shows that the absorption of hydrogen in over-pressurized hydrogen atmosphere is more effective, than chemical treatment and charge by electrolytic processes. The formation of hydrogen hosting sites occurs even with the standard fabrication method, without the need of any of the above mentioned treatments. Annealing under different inert gases are of theoretical interest also, since we show evidence of different translational movement restrictions according to the nature of the inert gas. Even more important, we show that in some circumstances, the anode–cathode current used to measure the stored hydrogen in vapour grown carbon fibres, may not constitute a reliable methodology.

Introduction

Our modern society demands means of producing energy which do not have a negative impact on the environment. This is critical in the case of the transport industry due to its widespread use and large amount of contaminants it produces. As the most abundant element on earth and due to the production of water as the only byproduct, hydrogen constitutes the natural choice towards an economy based on a clean renewable energy [1]. Nevertheless, this abundance is misleading, since more than 99% of hydrogen is chemically

* *Corresponding author*. Departamento de Física Aplicada, Facultad de Ciencias, Avenida Francisco Tomás y Valiente 7, Universidad Autónoma de Madrid, 28049 Madrid, Spain. Tel.: +34 914974021.
E-mail address: David.MartinyMarero@uam.es (D. Martín y Marero).
http://dx.doi.org/10.1016/j.ijhydene.2014.06.049

bound to oxygen in water or to carbon in different hydrocarbons, and only the rest is available as molecular hydrogen. On the other side, although the technique for obtaining molecular hydrogen gas is well developed, the problem of its storage and recovery has not been solved for its use in mobile applications [2]. As its storage in liquid form is economically unreasonable, the solution is the synthesis of hydrogen storage materials which capture and store it via adsorption mechanisms. These materials should be highly efficient, and in particular, able to store in excess of 6.5 wt% to be adequate for the mobile industry [3] according to the standards of the Department of Energy of the United States.

As a consequence, an intense international research activity is in progress to identify and develop systems able to perform these tasks. Among these systems, there are two main promising groups: metal hydrides [4,5] and simple carbon based materials [6]. Concerning the latter, it was very soon realized that their adsorption capacity could be significantly improved by their surface activation to achieve a maximum value close to 1 wt% under a pressure of 10 MPa [7], and therefore, far from the desired 6.5%. For this reason, research has focussed on the possibilities of carbon based nanostructures such as: single and multiwalled carbon nanotubes [8–10], fullerenes [11], graphite intercalation compounds [12] and vapour grown carbon fibres [13].

Although with poor initial results [14], the use of some of the variants, as the intercalated compounds, greatly improved the perspectives of high technology nanocarbons [15]. In the case of multiwalled carbon nanotubes, a different approach is followed, where advantage is taken of the multiple structural defects, present as well in any type of amorphous carbon, which allows for a larger hydrogen storage. For multiwalled nanotubes, it has been found that H_2 could be adsorbed and desorbed at room temperature, with an hydrogen storage capacity proportional to the nanotube diameter and with up to a 4.6% in weight [9]. The responsible mechanism profits from the imperfections in the most external layers, where H_2 accumulates in large voids. This suggests that the thicker fibres should be selected in order to increase storage capacity, and therefore, the study of new ways to increase this thickness, can prove of paramount importance to achieve the desired hydrogen storage. As will be explained later, this is also the case for vapour grown carbon fibres due to its similar structure in scales.

The growing of these fibres from hydrocarbon gases, has been known and even patented [16] from the late nineteen century, but even so, the available explanations concerning the formation and growing processes are not fully comprehended. The fibres are grown in a chemical reactor, which is basically a heated cylindrical reactor tube, by pyrolysis of hydrocarbons over catalytic particles of transition metals. In fact, there is a strong relationship between the resulting fibre structure and the particles, with experiments showing that the size of the catalyst particle determines the diameter of the grown carbon fibre, whereas the particles concentration determines the fibres yield [17]. In fact, there is also evidence that the presence of temperature gradients in the particles is at the heart of the fibre growth itself [18].

In general, we can summarize the production of vapour grown carbon fibres as a mixing process of three main components, in the chemical reactor: i) a precursor atmosphere made of an hydrocarbon gas and hydrogen; ii) a vapour containing the transition metal that will act as catalytic, usually iron from $Fe(CO)_3$ or $Fe(NO_2)_3$; iii) and optionally, a sulphur containing gas, usually H_2S, which enhances the catalytic properties of the transition metal, improving the fibre yield. In the reactor, the hydrocarbon gas plus hydrogen is allowed to flow in the presence of the iron containing compound particles and the sulphur added gas. First, the iron compound decomposes, producing iron particles, which are carried along with the flowing gases. Afterwards, the hydrocarbon decomposes and the produced carbon is attached to the iron catalyst particle, forming submicron carbon fibres. The subsequent deposition of graphene platelets forms cylindrical layers around the initial fibre, up to an approximate thickness of half a micron.

Given the presence of so many variables: components, temperature, gas flow speed or gas residence time, it should not come as a surprise the possibility to produce a wide range of different types of fibres by changing the production routine. In general, the most convenient production conditions are about 1373 K and an atmosphere of 30–40% of hydrocarbon and 70 - 60% of hydrogen [19]. In particular, the choice of the hydrocarbon precursor is a main aspect, because depending on the composition of the precursor gas, the grain of the solid carbon produced have different sizes [20] and different hydrogen content [21].

Vapour grown carbon fibres have a duplex structure consisting on: the primary filament, which constitutes the inner core and is made of a catalytic phase based on linearly textured coronene, and a second phase, constituted by a coating of a more disordered pyrolytic carbon deposit [22,23]. The inner core itself has a tree trunk structure, id est, parallel concentric layers, whereas the coat is formed by a carbonaceous material, mainly graphite scales, with poor structural order. Therefore, there are two completely different regions, both of them able to store hydrogen on the basis of distinct mechanisms and with a rich variety of possible hydrogen adsorption sites on each case and in the region between.

Nevertheless, perhaps the most difficult problem to evaluate the effect of the different methods used to increase the ability of the material to store hydrogen, is the lack of a reliable technique to measure the hydrogen content in the fibres. A recent study [24] has shown the importance of small errors and different methods and definitions in the quantification of gas phase hydrogen sorption measurements, when the most common methods are used. Traditionally, the hydrogen content is measured using a volumetric method, that is, measuring the amount of gas released by the sample [25,26]. Another widely used method is thermo-gravimetric analysis, where the sample is placed in an inert gas atmosphere and the temperature is changed in a controlled manner [27,28].

Besides the large uncertainties analysed in Refs. [27] and [24], the drawbacks associated to these types of techniques, is the occlusion of the hydrogen in different locations of the sample, with corresponding different adsorption and desorption energies, an information which is lost with volumetric and gravimetric measurements. This constitutes a severe handicap, since the knowledge of the location of the hydrogen and the different associated energies, implies

Please cite this article in press as: Martín y Marero D, Madroñero A, Critical findings during the optimisation of hydrogen storage in vapour grown carbon fibres, International Journal of Hydrogen Energy (2014), http://dx.doi.org/10.1016/j.ijhydene.2014.06.049