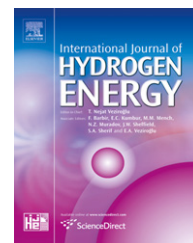


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Scale-up activation of carbon fibres for hydrogen storage

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ABSTRACT

In a previous study, we investigated, at a laboratory scale, the chemical activation of two different carbon fibres (CF), their porosity characterization, and their optimization for hydrogen storage [1]. In the present work, this study is extended to: (i) a larger range of KOH activated carbon fibres, (ii) a larger range of hydrogen adsorption measurements at different temperatures and pressures (i.e. at room temperature, up to 20 MPa, and at 77 K, up to 4 MPa), and (iii) a scaling-up activation approach in which the obtained activated carbon fibres (ACF) are compared with those from laboratory-scale activation. The prepared samples cover a large range of porosities, which is found to govern their ability for hydrogen adsorption. The hydrogen uptake capacities of all the prepared samples have been analysed both in volumetric and in gravimetric bases. Thus, maximum adsorption capacities of around 5 wt% are obtained at 77 K, and 1.1 wt% at room temperature, respectively. The packing densities of the materials have been measured, turning out to play an important role in order to estimate the total storage capacity of a tank volume. Maximum values of 17.4 g l^{-1} at 298 K, and 38.6 g l^{-1} at 77 K were obtained.

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1. Introduction

Hydrogen is considered an important vector for the future energy market. In this context, the storage of hydrogen plays a key role for mobile applications such as cars [2]. In the scope of the FreedomCAR initiative, the U.S. Department of Energy (DOE) specified a number of technological requirements which need to be achieved for a successful transition to hydrogen-based transportation [3]. The established targets set limits to e.g. the refilling time, the cycle life-time, the costs, and the densities of the storage system [3]. Ever since, these guidelines actuated as an important stimulation for research in this field. However, despite the worldwide effort of scientists and engineers, none of the current technologies meets all of these demands. Usually, in the research of materials for hydrogen storage, special attention is drawn to the gravimetric and volumetric densities. Especially in the case of

introducing hydrogen technology into existing car designs, volumetric restrictions to the tank need to be taken into account [4]. Lately in 2009, the DOE revised their system density targets which are now based on light-duty vehicles and reduced them to 4.5 wt.% and $28 \text{ g}_{\text{H}_2} \text{ l}^{-1}$ (target for 2010), 5.5 wt.% and $40 \text{ g}_{\text{H}_2} \text{ l}^{-1}$ (target for 2015), and 7.5 wt.% and $70 \text{ g}_{\text{H}_2} \text{ l}^{-1}$ (ultimate target), respectively [5].

Presently, a number of methods and technologies are investigated regarding their hydrogen storage performance. Most of the current hydrogen car prototypes are based on high pressure vessels. This is a relatively simple and cost-efficient technology. However, the tanks occupy a lot of space due to low storage densities, and security concerns exist because of the high pressures. For the compression, around 12% of the stored energy is consumed in order to reach 35 MPa, and 15% for 70 MPa, respectively [4]. Another possibility, which is favoured by some car manufacturers, is to store hydrogen as

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a liquid at cryogenic temperatures [6]. Although liquid hydrogen has a high density, the density of the storage system is reduced by the tank isolation and auxiliary devices. Even so, the isolation remains imperfect, causing some of the stored hydrogen to constantly evaporate. This fraction needs to be removed from the tank in order to avoid increasing pressures which would destroy the tank. In addition, a significant amount of its chemical energy (approximately one third) is needed in order to liquefy the hydrogen [3,7]. A third method for increasing the low density of hydrogen is to bind it to materials. Because of the wide range of possible materials and reaction mechanisms, their categorization is sometimes debatable. However, one can distinguish between chemical and physical methods. In chemical methods, the H_2 molecule is broken, and the elementary H atoms form chemical bonds with other atoms. Usually, for achieving reasonable gravimetric storage densities, high binding enthalpies are involved. These lead to a considerable amount of heat that needs to be transferred during charging and discharging [4,8,9]. Thus, for a typical heat of formation of $25 \text{ MJ kg}_{H_2}^{-1}$, a heat exchanger of several hundreds of kW would be necessary [4]. This significantly reduces the energy efficiency of the whole process, e.g. in the case of MgH_2 by a 30% [10]. In physical methods, in contrast, the H_2 molecules are attracted to the surface of highly porous materials by Van-der-Waals interactions. Here, relatively low adsorption enthalpies of around $4\text{--}8 \text{ kJ mol}^{-1}$ are involved, avoiding the need for active cooling devices [11,12]. However, additionally to filling a tank with the adsorbent, high pressures and/or low temperatures are necessary in order to favour this physisorption process. A promising candidate among the different adsorbent materials are activated carbons. Through activation, highly porous materials with large specific surface areas can be prepared [13–17]. Due to their high porosity, activated carbon materials are able to adsorb considerable amounts of hydrogen [1,7,12,18–34].

Carbon is the basis of organic compounds and is therefore an abundant element on earth which can be obtained from numerous sources. Thus, some of the advantages of carbon-based hydrogen storage materials are their high availability and low costs [18,35]. After all, millions of tons of hydrogen storage material will be necessary in order to replace the number of existing cars with others based on hydrogen technology [4,36]. In this sense, it is important to investigate the possibility of producing activated carbon materials on a larger scale [4,32]. However, it is a difficult task to produce highly specialized adsorbents in large amounts. Thereby, the heat treatment is the most crucial step which requires careful control [16]. In addition, information about scale-up synthesis is poorly described in the open literature, due to the confidential character of commercial production data [37]. Recently, El Qada et al. compared physical activations of bituminous coal in a tube furnace and in a rotary kiln [38]. For hydrogen purification, Lopes et al. compared physical activation of activated carbons prepared at laboratory-scale with those obtained from a scale-up process [39]. The porosities in those approaches were reproducible within a margin of less than 6% [38], and around 9% [39], respectively.

The objective of the present work is twofold:

On the one hand, a scale-up approach is performed in order to produce optimized activated carbon fibre materials for

hydrogen storage. Thereby, results obtained in a previous study are taken into account. In this preliminary work, we investigated the chemical activation on laboratory-scale of two different carbon fibres which were carbonized at different temperatures (973 K and 1273 K, respectively), as well as their porosity optimization for hydrogen storage [1]. In the present study, the same two carbon fibre precursors are used for scale-up activation. The results from those activations are evaluated, and compared with those obtained from laboratory-scale activation. In our previous study, both, KOH and NaOH, were used as activating agents [1]. The present study is restricted to activations with KOH, because the activation process with KOH showed a higher yield in comparison with NaOH activation and featured a more appropriate, narrower porosity [1].

Secondly, extensive hydrogen adsorption measurements are carried out at both, room temperature (up to 20 MPa) and 77 K (up to 4 MPa), respectively. The adsorption amounts, obtained in a wide range of samples, are correlated with their narrow and total microporosities. Furthermore, the packing densities of all the samples prepared are measured, and the total hydrogen storage, which is the most important parameter from an application point of view, is assessed. As a result, the total hydrogen storage includes, apart from the adsorbed phase, the hydrogen that is compressed inside of the void space. Thereby, the importance of the packing density of the material and of its measure is pointed out.

Finally, it is important to note that, in difference to other studies [7,12,18,23–34], all the samples of the present study come from a given precursor. Thus, the possible effects of other pristine sample properties like for example the materials macro-structure, ash-content, etc. are eliminated.

2. Materials and methods

2.1. Materials

The two carbon fibre (CF) precursors, produced from coal-tar pitch, were provided by Osaka Gas Co., Ltd (Osaka, Japan) and carbonized at different temperatures: Donacarbon S-241 at 1273 K, and Donacarbon SL-242 at 973 K, respectively. In order to activate them, the CFs were physically mixed with corresponding amounts of activating agent. For all activations, potassium hydroxide pellets (PRS Panreac) were used as activating agent. After the activation process, the activated carbon fibres (ACF) were repeatedly washed and vacuum filtered, in order to remove the by-products of the reaction. First, 5 M solution of hydrochloric acid, and then distilled water were used for washing. Finally, the washed ACFs were dried at 383 K overnight.

Concerning the nomenclature of the investigated materials, the first part of the sample names indicates the precursor which was used and corresponds to its carbonization temperature in centigrades. Thus, “D1000” corresponds to the samples that are based on the fibres which were carbonized at 1000 °C (Donacarbon S-241), and “D700” to those which were carbonized at 700 °C (Donacarbon SL-242), respectively. For denomination of the ACFs, a suffix like “-KX” is used, whereby the term “X” indicates the KOH-to-CF ratio

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