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Preparation and hydrogen storage of activated rayon-based carbon fibers with high specific surface area

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ABSTRACT

Activated carbon fibers were prepared from rayon-based carbon fibers by two step activations with steam and KOH treatments. Hydrogen storage properties of the activated rayon-based carbon fibers with high specific surface area and micropore volume have been investigated. SEM, XRD and Brunauer–Emmett–Teller (BET) were used to characterize the samples. The adsorption performance and porous structure were investigated by nitrogen adsorption isotherm at 77 K on the base of BET and density functional theory (DFT). The BET specific surface area and micropore volume of the activated rayon-based carbon fibers were 3144 m^2/g and 0.744 m^3/g, respectively. Hydrogen storage properties of the samples were measured at 77 and 298 K with pressure-composition isotherm (PCT) measuring system based on the volumetric method. The capacities of hydrogen storage of the activated rayon-based carbon fibers were 7.01 and 1.46 wt% at 77 and 298 K at 4 MPa, respectively. Possible mechanisms for hydrogen storage in the activated rayon-based carbon fibers are discussed.

1. Introduction

Hydrogen energy system is expected to progressively replace the existing fossil fuels in the future because of its cleanness and high energy density. One potential use of hydrogen lies in powering zero-emission vehicles via a proton exchange membrane fuel cell to reduce atmosphere pollution. Hydrogen can be converted to electricity with emission of only water with very high efficiency [1–3]. However, hydrogen is a gas with critical temperature of 33.19 K. Above this temperature, hydrogen cannot be liquefied and is inconvenient to be stored and transported. To achieve this goal feasible onboard hydrogen storage systems have to be developed.

The US Department of Energy (DOE) Hydrogen Plan has set a standard for this discussion by providing a commercially significant benchmark for the amount of reversible hydrogen adsorption. The benchmark requires a system-weight efficiency (the ratio of stored hydrogen weight to system weight) of 6.5 wt% hydrogen and a volumetric density of 62 kg H_2/m^3, since a vehicle powered by a fuel cell would require more than 3.1 kg of hydrogen for a 500 km range [1].

As a result, hydrogen storage materials have attracted intense research interest [4,5]. The hydrogen storage properties of different materials have been reported, for example metal hydrides, metal organic frameworks and carbon materials [6–10]. Of these, carbon materials receive special attention because they are cheap and easy to obtain, and also because they have good recycle properties. Tremendous interests have been aroused by the discovery [11] and reproduction of high hydrogen adsorption capacity in carbon nanotubes and other low-dimensional carbon materials [12–18]. Various carbon materials have been suggested, such as carbon nanotubes, carbon nanofibres, activated carbon, ordered porous carbon, etc. [19–22]. Physical adsorption generally accounts for the way that hydrogen is stored in carbon materials [23]. Several factors are considered to be related to the storage, for example, the pore structure and the special surface area [19,24]. In this paper, activated carbon fibers with high specific surface area and micropore volume were prepared from rayon-based carbon fiber by physical and chemical activations. The hydrogen storage of the activated rayon-based carbon fibers (ARCF) was investigated.

2. Experimental

The precursor was rayon-based carbon fiber. The activated carbon fibers were prepared from rayon-based carbon fibers by two step activations with steam and KOH treatments. The rayon-based carbon fibers were first activated by steam at 900 °C for 1.0 h, which is designated as ARCF1. Then the activated rayon-based carbon fibers (ARCF1) and KOH (the weight ratio is 1:8) were mixed with distilled water in a nickel crucible and

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subsequently activated at 850 °C for 1.0 h in N_2 atmosphere. The resulting material was neutralized with 2 M hydrochloric acid and then thoroughly rinsed with deionised water until the pH of the filtrate was about 6–7. The activated rayon-based carbon fibers were dried at 120 °C under air atmosphere for 12 h, which is designated as ARCF2.

Scanning electron microscope (SEM) and high resolution scanning electron microscope (HRSEM) images were taken with field-emission scanning electron microscopy (SEM, Hitachi S-4700). Powder X-ray diffraction (XRD) was tested with a Rigaku D/MAX-3CX diffractometer using the $K\alpha$ line of Cu as a radiation source.

Specific surface areas were taken using N_2 at 77 K with a COULTER SA 3100 apparatus after outgas at 573 K for 120 min. After outgas at 573 K for 2 h, hydrogen storage properties of the samples were measured at 77 and 298 K with pressure-composition isotherm (PCT) measuring system based on volumetric method, Suzuki Shokan Corporation. Before each test, hydrogen at 4 MPa was charged into the equipment for 12 h and the pressure changed no more than 0.003 MPa, which demonstrated there is no leaking. In the experiment, the sample was put into the reaction container, and the container was immersed into liquid nitrogen carried in a Dewar vessel. In this way, the hydrogen storage properties at 77 K were obtained.

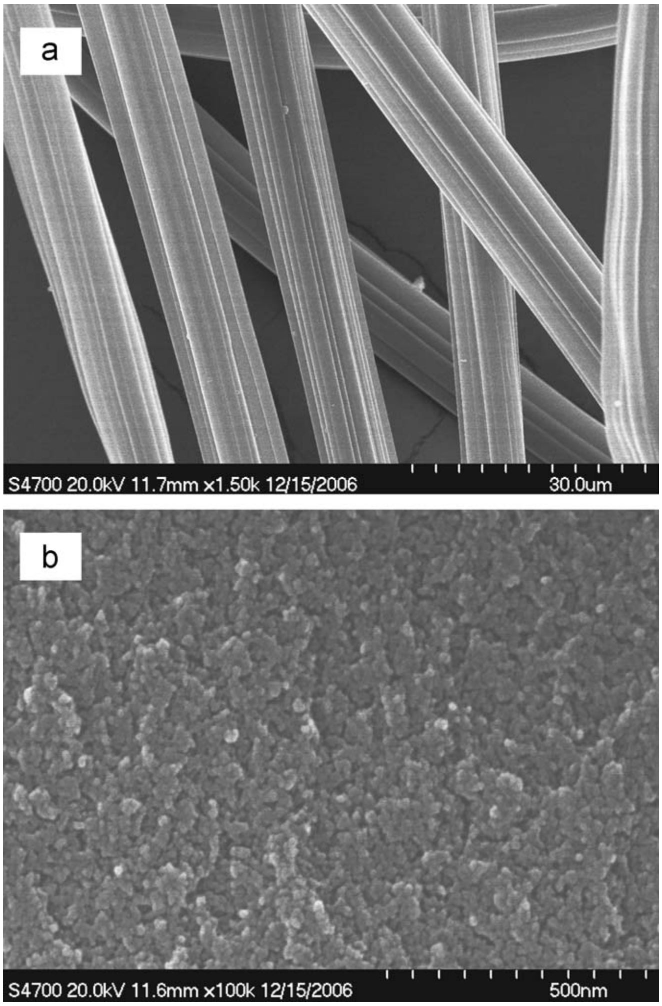

Fig. 1. SEM (a) and HRSEM (b) images of ARCF1.

3. Results and discussion

SEM and HRSEM images of ARCF1 and ARCF2 are shown in Figs. 1 and 2. The activated rayon-based carbon fibers are long fibers with smooth surfaces, whereas HRSEM images of the samples show that the surface states of the activated rayon-based carbon fibers are different. The surface of the ARCF1 sample is smooth, whereas the surface of ARCF2 sample is rough and has many holes with tens of nanometers in diameter. To get more information of the difference, XRD was used, and the XRD patterns are shown in Fig. 3. The XRD results show that ARCF1 is a semi-crystallized sample and ARCF2 is a completely amorphous one.

The pore structures of the activated rayon-based carbon fibers were further analyzed using nitrogen sorption technique. Fig. 4 shows the nitrogen adsorption/desorption isotherms of the ARCF1 and ARCF2 samples. The adsorption performance and porous structure were investigated by nitrogen adsorption isotherm at 77 K on the base of Brunauer–Emmett–Teller (BET). With these curves, the pore structures of the samples are estimated [25,26]. The pore size distributions of ARCF1 and ARCF2 samples are shown in Fig. 5. ARCF1 sample has large nitrogen adsorption and the curve belongs to type-I of BET curves, and therefore, ARCF1 sample is a microporous material, not a smooth one as shown by SEM. ARCF2 has larger nitrogen adsorption than ARCF1, so combining the data given by the equipment, we know that the pores of ARCF2 sample are made up of micro-, meso- and macropores. Based on the results above, we conclude that corrosion with KOH at 850 °C made ARCF2 amorphous and enlarged its pores. The BET specific surface area and micropore volume are 3144 m^2/g and 0.744 m^3/g for the ARCF2, and 1256 m^2/g and 0.359 m^3/g for the ARCF1, respectively. Obviously, surface areas decrease with crystallization of the samples.

The capacities of hydrogen storage of the ARCF1 and ARCF2 samples at 298 K are presented in Fig. 6. Both adsorption lines seem to be linear. The reason for this is the low amount of hydrogen uptake. There is no hysteresis in all samples, indicating that adsorbed hydrogen can be desorbed reversibly [27,28]. ARCF2 sample showed higher hydrogen adsorption than ARCF1 sample. This is believed to be due to the higher specific surface area and micropore volume of ARCF2 than those of ARCF1. The hydrogen storages of the ARCF1 and ARCF2 samples were 0.62 and 1.46 wt% at 4 MPa and 298 K, respectively.

As is well known, carbon materials store hydrogen by physical adsorption, and this effect reduces drastically with increasing temperature [5]. Therefore, hydrogen storage properties of the activated rayon-based carbon fibers were measured at liquid nitrogen temperature (77 K). The hydrogen adsorption curves of the activated rayon-based carbon fibers are shown in Fig. 7. The hydrogen storages of the ARCF1 and ARCF2 samples were 3.41 and 7.01 wt% at 4 MPa and 77 K, respectively. It can be seen from the graph that the curves do not belong to any type of the five BET curves. Compared with BET data, the hydrogen storage is not proportional to the specific surface area and the storage increases almost linearly with pressure when it is above 1.0 MPa. These curves cannot be simply explained by a single kind of mechanism. Therefore, based on other researchers' work [21,24,29–31] and our own results, we suggest that the hydrogen storage in carbon materials has four types of mechanisms. I-type, the hydrogen liquefies in the micropores of the materials; II-type, the hydrogen is adsorbed on the surface of the carbon particles and the inner wall of meso- and macropores; III-type, the hydrogen molecules permeate in between the graphite layers; IV-type, the hydrogen is stored in the space between the carbon particles. Of the four types of storages, the I-, II- and III-type storages are