

Hydrogen storage of catalyst-containing activated carbon fibers and effect of surface modification

Ikpyo Hong, Seong-Young Lee, Kyung-Hee Lee, Sei-Min Park

Carbon Materials Research Group, Research Institute of Industrial Science & Technology, 790-600, Pohang, KOREA

Introduction

The hydrogen storage capacities of many kind of carbon nano materials have been reported with possibility and improbability[1,2]. It is reported that specific surface area of carbon nano material has not a close relation to hydrogen storage capacity. This result shows that there is difference between specific surface area measured by isothermal nitrogen adsorption and direct measurement of adsorption with hydrogen and suggests that the carbon material with relatively low specific surface area can have high hydrogen storage capacity when they have effective nano pore.

In this study, petroleum based isotropic pitch was hybridized with several kinds of transitional metal base organometallic compound solved with organic solvent and spun by electrospinning method. The catalyst-dispersed ACFs were prepared and characterized and hydrogen storage capacity was measured. The effect of surface modification of ACFs by physical and chemical treatment was also investigated.

Experimental

The isotropic precursor pitch prepared by nitrogen blowing from naphtha cracking bottom oil was hybridized with transitional metal based acetyl acetonates and spun by solvent electrospinning. Tetrahydrofuran and quinoline were used as solvent with various mixing ratio. High voltage DC power generator which could adjust in the range of 0-60,000V and 2mA maximum current was used to supply electrostatic force. At the solvent electrospinning, solvent mixing ratio and pitch concentration, voltage and spinning distance were varied and their influences were investigated. The catalyst dispersed electrospun pitch fibers were thermal stabilized, carbonized and activated by conventional heat treatment to activated carbon fiber. Prepared fibers were observed by high resolution SEM and pore properties were characterized by Micromeritics ASAP2020 model physisorption analyzer.

Hydrogen storage capacities were measured by equipment modified from Thermo Cahn TherMax 500 model high pressure thermogravimetric analyzer under pressure range from vacuum to 10MPa. Sample was pretreated by degassing at 150°C for 5 hours and cooling overnight under 10⁻⁴ torr vacuum and measurement of hydrogen adsorption was performed under pressure ranged 10⁻⁴ torr-10MPa. The hydrogen storage amount is calculated from measurement weight change with respect to pressure by subtracted buoyancy measured by reference test which performed measurement of weight reading change of volume-known glassy carbon with respect to the pressure. The sample volume was calculated from density measured with Micromeritics Accupyc 1330 automatic helium pycnometer. Surface modification of adsorbents was performed by physical and chemical treatment such as ball milling or acid treatment and also analyzed as mentioned above.

Results and discussion

Prepared ACFs with various catalysts were obtained with form of web which filament diameter is ranged 1-5 μ but spinnability of pitch solution was relatively decreased comparing with pure pitch solution owing to decrease of viscosity. The optimum conditions were 30-40wt.% for pitch/solvent concentration, 13-30kV for spinning voltage and 13-17cm for tip to collector distance. Specific surface area measured by nitrogen adsorption isotherm of ACFs was ranged 100-3000m²/g and pore size distribution of ACFs were varied with respect to species and contents of catalyst which indicate similar result by catalyst dispersed melt spun ACFs.[3]

Hydrogen storage capacities of ACFs showed ranged 0.31.0% in weight at 10MPa in room temperature and Fig.1 shows effect of hydrogen storage by surface modification. Hydrogen storage capacity was decreased by ball milling and increased by acid treatment. It is assumed that pore structure deforms by ball milling but effective hydrogen storage capacity increases with edge exposure by acid treatment. But this result was obtained by mild treatments and still requires further in-depth study about relationship between hydrogen storage and structure change by tests under various conditions including severe conditions.

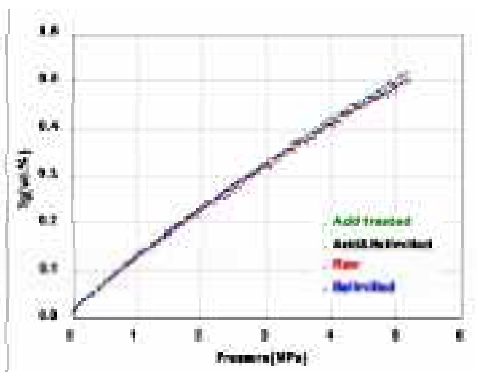


Fig.1 Effect on H₂ storage by surface modification of raw ACF (SSA 286W/g, micropore SA 2610m²/g), ballmilled for 96hrs (SSA 2330m²/g, micropore SA 217W/g), HNO₃ treated (SSA 2980m²/g, micropore SA 2700m²/g), acid and ballmilled (SSA 2480m²/g, micropore SA 2320m²/g)

[1] M. A. de la Casa-Lillo, et al.; J. Phys. Chem. B, 106, 10960, 2002

[2] H. Cheng, Quan-Hong Yang, Chang Liu; Hydrogen storage in carbon nanotubes, Carbon, 39, 1447, 2001