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Studies on the correlation between nanostructure and pore development of polymeric precursor-based activated hard carbons: II. Transmission electron microscopy and Raman spectroscopy studies

Jin Baek[a,b], Hyung-Shik Shin[b], Dong Chul Chung[a], Byung-Joo Kim[a,*]

[a] R&D Division, Korea Institute of Carbon Convergence Technology, Jeonju 54853, Republic of Korea
[b] Department of Chemical Engineering, Chonbuk National University, Jeonju 54896, Republic of Korea

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ABSTRACT

In a previous study, we reported on activated polymer-based hard carbons (APHCs), which were prepared using CO_2 activation and characterized according to activation conditions, including textural properties such as specific surface area and pore volume. This paper was focused on the correlation between nanostructure and pore development of APHCs by using Cs-corrected-field emission transmission electron microscopy (Cs-corrected FE-TEM) and Raman spectroscopy to supplement the in-depth explanation. In the TEM analysis, the APHCs were observed to contain slit-shaped pores (SPs) and little cylindrical pores (CPs). And Raman spectroscopy was used in order to determine the degree of development of the crystal size (L_a) in the APHCs. The size of L_a increased with increasing activation time until it was nearly 3 nm. These small crystallites might cause the SPs development, resulting in the high micropore volume of the APHCs. From a result of Raman analysis, it was confirmed that the L_a value and the ratio of I_D/I_G value were in a proportional relation. The reason for this relation is that the L_a value has grown up to about 3 nm, which is consistent with the Ferrari equation.

Introduction

With the rapid exhaustion of fossil fuels and the increasing emissions of CO_2 and other environmental pollution, there are growing demands for research to develop more efficient, clean and sustainable pro-environmental energy sources, as well as new technologies for more efficient pollutant removal, carbon fuel cells, gas storage, and cell biology [1–4].

To address these environmental pollution problems, a considerable amount of research has focused on the investigation and applications of carbon materials. Carbonaceous materials, activated carbon [5,6], carbon nanotubes [7,8], graphene [9,10], and carbon microspheres [11,12] have been widely studied. Among the carbonaceous materials, hard carbon based activated carbons (ACs) have been widely used in the environmental sector due to their outstanding gas and liquid adsorption capacities, which are determined by the material's structure and porosity characteristics [13–16]. In particular, polymer-based hard carbon has attracted increasing attention, as it provides several additional advantages. It produces hardly any ash, has high carbon content, its non-crystal pore structure characteristic provides a high specific surface area (SSA) of 1000–3000 m^2/g, and it has few side reactions in the adsorption process [17–21]. Among these many advantages, the high SSA of the ACs is particularly valuable for environmental and energy storage applications.

The high SSA results from the existence of micropores in the material. Such pores can be distinguished according to their shape. Slit pores (SPs) are formed between parallel plates, and cylindrical pores (CPs) are formed in a region which is connected by pore channels, or polygonally, by more than two carbon layers. Theoretically [22,23], the SPs help to form the high SSA. Kaneko et al. [24] reported a SPs model that explained the role of the SPs in the high SSA of laminated graphite crystalline planes.

Traditionally, the pores in ACs have been characterized by various techniques which mostly depend on the pore's size. Nanometer sized pores such as micropores and mesopores are identified by analyzing gas adsorption isotherms, mostly of N_2/77 K. The gas adsorption method can detect only open pores, that is, those which can accept gas molecules.

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[*] Corresponding author. Fax: +82 63 219 3729.
E-mail address: kimbj2015@gmail.com (B.-J. Kim).

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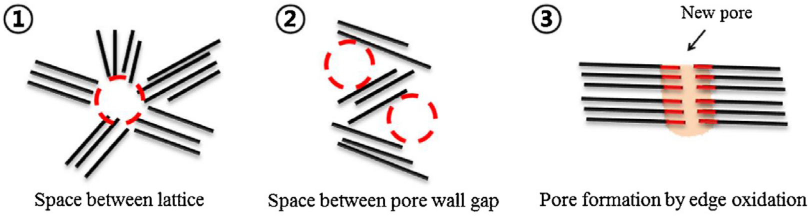

Fig. 1. Models of pore generation and development in hard carbon structure.

Meanwhile, X-ray diffraction (XRD) has the advantage of being able to identify latent pores, including closed pores. And generally, it is possible to measure the layer distance of porous carbon material by using XRD. Pores in porous carbon are generated in three forms as follows (Fig. 1);

When XRD is used, it is possible to indirectly confirm the tendency of pore corresponding to ②, and it can be utilized as a useful tool for pore analysis of ultra-micropore ($<$0.7 nm) [25,26]. To obtain highly accurate grain sizes (crystalline size), TEM and Raman techniques can also be employed to support the XRD results [27–33].

In a previous study [34], activated polymer-based hard carbons by a CO_2 activation (APHCs) were determined to have a high micropore volume. This was found to be due to the presence of a large number of micropores, depending on activation conditions. Accordingly, analyses of the pore characteristics of APHCs were performed using the Brunauer–Emmett–Teller (BET) [35,36], Barrett–Joyner–Halenda (BJH) [37], and Horváth–Kawazoe (HK) [38] equations.

In this study, we employed Cs-corrected-field emission transmission electron microscopy (Cs-TEM), Raman, and XRD techniques in order to fully understand the pore development in APHCs from the aspect of nano-structural and textural developments. A suitable pore development mechanism is proposed based on the correlation between crystallite size and the composition of the SPs and CPs, with activation conditions.

Experiment details

Materials

Polymer-based hard carbons were supplied by Aekyung Petrochemical Co., Ltd. Activated hard carbon samples of 3 g were produced by physical activation at 900 °C and then held for 20–60 min under CO_2 gas flow at 500 cc/min at a heating rate of 10 °C/min. All gases had a high purity of 99.999%. And all samples are kept in desiccator at 25 °C [34].

Structure and morphology characterization

To observe the microstructures of the samples, Cs-corrected-field emission transmission electron microscopy (Cs-corrected FE-TEM, 200 kV) and selected area electron diffraction (SAED) patterns were obtained with a JEM-ARM200F microscope (JEOL, Japan).

Raman spectroscopy is a very effective method to investigate the intimated bonding structure of carbon. Though there is still discuss on the exact relationship between the Raman spectra and atom vibration, the method in this paper is used to distinguish the domain size in nanocrystalline materials. The measurement area was chosen near to the mark point using a camera in a Raman microscope (NTEGRA, NT-MDT, UK). Micro-Raman spectroscopy measurements were taken at room temperature in Raman scattering geometry with a change in polarizability. All the samples were prepared and measured as powder. Raman was performed using green (532 nm) laser excitation wavelength, and a magnification of ×100. Scans were taken in the range of 500–4000 cm^{-1}. And Lorentzian fitting was performed to calculate the full width at half maximum (FWHM).

The textural properties of the APHCs were conducted by conventional N_2/77 K adsorption isotherms. Following analysis, each sample was vacuum degassed for 5 to 6 h while maintaining a residual pressure below 133.32 Pa at 573 K. Using BELSORP-max (BEL JAPAN, Japan), the adsorption rate of the N_2 gas was measured in relation to relative equilibrium adsorption pressure (P/P_0) at 77 K. The SSA was derived from the adsorption isotherm based on the Brunauer–Emmett–Teller (BET) equation, and pore distribution has been characterized using the Horváth–Kawazoe (HK) and Barrett–Joyner–Halenda (BJH) equations. Also the shapes of pore development, such as slit and cylindrical, were studied by TEM and non-local density functional theory (NLDFT) [39] methods.

Results and discussion

Characterization of changes in the surface and pore shape of APHCs

Analyzing electron diffraction images formed by the interference effect of crystals and electrons can reveal the arrangement of a particular crystal unit cell. The theory of electron diffraction can be simply explained by Bragg's law.

$$n\lambda = 2d\sin\theta$$

where n is an integer (1, 2, 3 etc.), the reflected waves from different layers are perfectly in phase with each other, λ is the wavelength of the rays, d is the spacing between layers of atoms, and θ is the angle between the incident rays and the surface of the crystal. For electron scattering (2θ), when the SAED is a much smaller value than the diffraction angle of the XRD, the value can be ignored. At SAED point, when the deviation of the diffracted beam is 2θ, a diffraction ring patterns are represented from the L (the L means particle size of a powder group). Also, the diffraction beam and incident beam differs as x.

$$x = L2\theta \cong L\frac{\lambda}{d}$$

Fig. 2(a) exhibits a SAED pattern which shows diffraction rings, and is a demonstration of the non-crystalline structure of polymer-based hard carbons (HC). The distance between the parallel carbon layers is large, indicating a disordered non-crystalline structure. This is also proved by the (002) and (10l) diffraction lines and by the blurred diffraction rings in the SAED patterns. The near diffraction line which appears in the transmission electron beam has a very small size for a fine crystalline structure. And from this orientation it can be seen that it has a non-crystalline structure. The results of SAED with TEM give further proof that the HC is difficult to graphitize.

Fig. 2(b) shows the Cs-corrected FE-TEM image of the HC. It can be seen that the HC sample has numerous pores already, before

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