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A Study on Pore Development Mechanism of Activated Carbons from Polymeric Precursor: Effects of Carbonization Temperature and Nano Crystallite Formation

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Highlights

- Pore development mechanisms of polymeric precursor-based ACs has been revealed.
- Steam activation was very effective for removing disordered structure and small crystallites.
- ACs exhibited very high specific surface area from 1760 to 2340 m^2/g.
- Specific capacitance of the ACs have a deep correlation with micropore volume fraction.

1. Introduction

Electric double-layer capacitors (EDLCs) have attracted considerable attention as efficient energy storage devices. Charge storage in EDLCs utilizes electrostatic adsorption of electrolyte ions at the electrode–electrolyte interface. An ideal electrode material is expected to possess a high specific surface area, an optimal pore size distribution, electric stability, and electric conductivity for fast transport of the electrolyte ions and charges [1].

Activated carbons (ACs) make up a porous carbon material that possesses unique electrochemical properties due to qualities such as a well-developed porous structure, high specific surface area, and high pore volume. ACs can be prepared from a wide range of raw materials including coal, pitch, biomass, and even polymeric resins. Polymeric precursors have specificity with a uniform chemical structure and can be able to be transformed to hard carbons which have size-controlled crystallites during the carbonization process. Polymer-based hard carbons with ordered crystallites can be converted to well-developed activated carbons with an optimized pore structure for the electrode materials of EDLCs [2].

In this work, activated polymer-based hard carbons (APHs) were prepared as a function of various carbonization temperatures to control the formation of nano-sized crystallites in hard carbons which are the precursors, and the activation mechanism for polymeric resin by steam activation were proposed as well. For application of APHs manufactured in this work, textural properties (specific surface area and micropore volume fraction) and electrochemical performance of the APHs were also evaluated.

2. Methods

2.1 Preparation of activated hard carbons

Polymeric precursors (Aekyung Petrochemical Co., Ltd.) were used as the starting materials. The polymeric precursors were heated (carbonized) from 600 to 900°C at 10 °C/min in a self-made cylindrical furnace (SiC heater) under N_2 gas (300 mL/min), and kept at a target temperature for 1 h to obtain polymer-based hard carbon (HC). Then, the gas flow was switched to H_2O at a rate of 0.5 mL/min while the temperature was raised to 900°C and held for 20 to 40 min. The samples were allowed to cool under N_2 gas (300 mL/min). The yield of activated sample was determined from the weight of the sample before and after activation.

2.2 Characterizations

The pore structure of the APHs was characterized by N_2 adsorption/desorption at 77K using a BELSORP-max (BEL JAPAN, Japan). The microstructure of the APHs was determined using a wide-angle X-ray diffractometer (WAXRD), employing a Rigaku SmartLab X-ray diffractor with customized auto-mount and a Cu Kα radiation source. Diffraction patterns were collected within the diffraction angles from 5° to 90° with a speed of 2 °/min.

2.3. Electrochemical measurements

The electrodes were prepared by coating aluminum foil with an aqueous APHs suspension (80 wt%) mixed with carboxy-methyl-cellulose binder (CMC, 6 wt%), a plasticizer (styrenebutyrene rubber (SBR), 4 wt%), and a conductive agent (carbon black, 10 wt%). All electrochemical measurements were carried out using organic electrolyte 1 M $(C_2H_5)_4NBF_4$/propylene carbonate at room temperature.

3. Results and discussion

Figure 1 shows the typical N_2 adsorption/desorption isotherms for APHs prepared in this work. The curve of APHs is classified as Type I by the IUPAC classification. The specific surface area of the APHs decreased with increase in activation temperature. The specific surface area and total pore volume of them APHs exhibited similar trend as well. The APH-6-9-4 sample was observed to have the best-developed mesopores volume than other samples. In the results, the high carbonization temperature can increase the size of crystallite of the hard carbons. This means that a low carbonization temperature can lead high specific surface area during the activation process. This means that pore size and volume can be controlled by the pre-carbonization conditions.

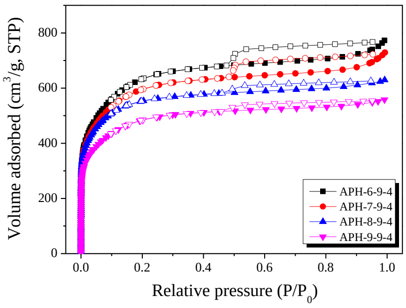

Figure 1. N_2/77 K adsorption and desorption isotherms of the activated hard carbons as a function of different carbonization and activation conditions

4. Conclusions

In this work, activated polymer-based hard carbon (APHs) electrodes with high double layer capacitance and good rate capability were prepared by optimizing the carbonization temperature prior to H_2O activation. The carbonization temperature has a significant effect on both the crystallite size and the electrochemical performances of APHs. From the charge-discharge characteristics, APHs-6-9-4 showed the best result (135 F/g) in all activated sample. A decrease of carbonization temperature results in higher specific surface area and larger pore size, and hence higher capacitance and better rate capability.

References

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Keywords
Polymer, Steam activation, Carbonization temperature, Electric double-layer capacitors.