ACTIVATION OF A CARBON BLACK USING POTASSIUM HYDROXIDE AND ITS ELECTRIC DOUBLE LAYER CAPACITOR

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Abstract

To prepare carbons for electric double layer capacitor, a carbon black was activated with potassium hydroxide (KOH). The capacity and microstructure of the carbons reacted with KOH ranging from 0 to 400% in weight were investigated. The activated carbon prepared with 350wt% was found to have the maximum surface area, 1500m2/g. However, the activated carbon prepared with 250wt% showed the maximum capacity, 9.3F/g. The capacity of this carbon was two times larger than the carbon prepared with 350wt%. The capacity was considered to be independent of the surface area. The crystallites were clearly observed in the carbons prepared with 350 and 400wt%.

Introduction

Electric double layer capacitor (EDLC) is defined as a condenser that accumulates electricity on surface between electrode and electrolytic solution. The small type of EDLC is used for the back up power supply of IC and LSI because the characteristics are excellent in that the working temperature range is wide, the lifetime is long, and the output is relatively high. Recent years, EDLC has come to be applied to hybrid cars and fuel cell cars [1,2]. Porous carbons with high surface areas such as activated carbon fiber are mainly used as an electrode material advantageous to adsorption and desorption of electrolytes. However, a development of EDLC with higher performance and higher capacity is desired. The selection of precursors from which porous carbons are produced with high yield is indispensable. The consistent supply of the raw material in quantity and quality must be possible. In this sense, carbon blacks are seemed to be a candidate as a precursor satisfying that condition. We attempted the possibility of production of activated carbon for electrode material through activation of carbon black using potassium hydroxide. In this paper, the activation effect by potassium hydroxide and the characteristics as EDLC are reported.

Experimental

Carbon black IP200 supplied by CABOT JAPAN Co. LTD. was used. The amounts of potassium hydroxide corresponding from 250 to 400wt% of carbon black in weight were added to the carbon black and then roughly mixed. Activation was performed at 750℃ for 1h in nitrogen in an electric furnace. The temperature was elevated at 2℃/min up to 750℃. After activation, the specimen was cooled in the furnace to room temperature, followed by dropping into water to dissolve the alkaline substances. The specimen was repeatedly rinsed with water and the adjustment of pH with 0.5M hydrochloric acid was conducted for neutralization. Resultant activated carbon black was evaluated in terms of surface area and pore size distribution through the measurement of nitrogen adsorption at 77K. Disk-like electrode with sizes of 0.3 mm thick and 10mm in diameter was prepared by compression-molding the activated specimen to which polytetrafluoroethylene (PTFE) of 5% in weight as a binder was added. Two disks are combined putting a separator between them and two artificial graphite plates as a collector material were attached to both sides. A two-electrode cell was fabricated to measure the electric double layer capacity. The electrolytic solution composed of Et3NBF4／PC (0.5mol/d m^3) was used. The charge and discharge were conducted under the conditions of 2.0V, 0.5A and 50mA, respectively.

Results and Discussion

Figure 1 shows the effect of addition amount of potassium hydroxide on the pore size distribution. The original carbon black is omitted because it has almost no pore volume compared to the activated specimens. It is remarkable that the pore volume in the micropore region increases with increasing amount of potassium hydroxide until 350wt%. In particular, the development in the pore ranging lass than 9 Å is notable. Almost no change between the original carbon and activated ones in the pore size distributions in the ranges of mesopore and macropore was confirmed. Figure 2 illustrates the surface areas as a function of potassium hydroxide amount. The maximum point at the 350wt% is seen. These data implies that the role of activation is not to expand but to rather develop the micropores. By TEM observation, the crystallites in the original carbon black were not confirmed. In the activated specimens, however, the crystallites existing around the outer surface of the primary particles could be observed. The clearness increased with increasing amount of the activator. In the 400wt% specimen, the crystallites in the inner portion of the primary particles were also observed. For this reason, the activator is considered to preferentially consume such carbons as amorphous part. It is concluded that numbers of micropore are increased by activation. However, the surface area of 400wt% specimen is less than that of the 350wt% specimen, which is thought to be due to the expansion of smaller micropores.

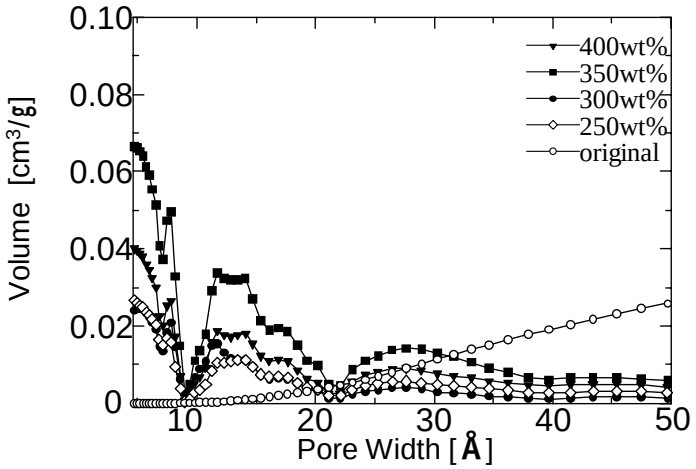

Fig.1 Pore size distributions of carbon black activated with various KOH ratios.

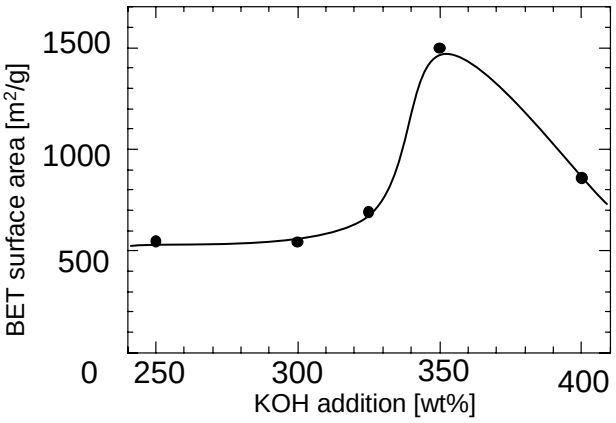

Fig.2 BET specific surface area of carbon black activated with various KOH ratios

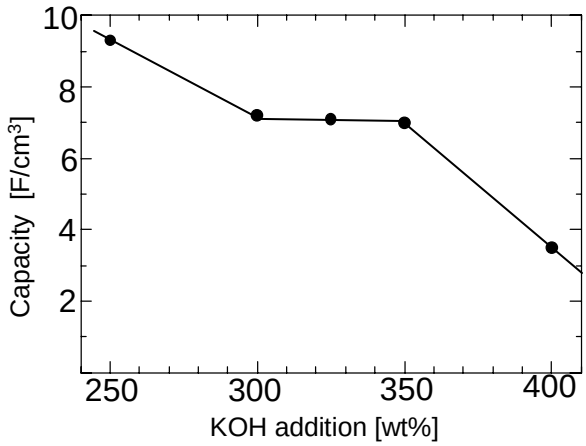

Fig.3 Change in electric double layer capacity of KOH activation

Figure 3 shows the relationship between the amount of the activator and the electric double layer capacity. The 250wt% specimen has highest value. A tendency for the capacity to decrease with increasing amount of activator is seen. This tendency is entirely different from that in Fig.2, indicating that the development of the micropores brought by activation does not contribute the capacity. Potassium hydroxide is known to develop the micropores relating to the high surface area. However, the resulting high surface area is reported to be not always proportional to the capacity. In general, it has been said that the pores larger than 10 Å may be effective. In this point, the activated carbon black is considered to have smaller pores in size as is seen in Fig.1. Also the contact among the respective particles might be insufficient. There is a possibility that adsorption and desorption are locally restricted in this experiments because the electrical resistance of carbons deeply activated is known to be significantly high.

References

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