The Preparation of Graphite Salts Using Anodic Oxidation Method

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Introduction

The acid anions (HSO_4^-, NO_3^-, ClO_4^- etc) can intercalate into the interlayer space of graphite and form graphite salts after the carbon atoms in the basal planes of the network are oxidized [1,2]. The industrial appilications of their useful characteristics. But there are still many problems which must be solved.

In making flexible graphite material with the usual immersion oxidation method, the strong oxidizing agents must be used and they will make the serious enrivonmental pollution [3,4]. Thus the anodic oxidation method in which the oxidizing agents are not adopted are now developed rapidly to displace the immersion oxidation method [5,6,7]. As well known, the compressibility, recovering property and mechanical strength of flexible graphite material depend on the expansion degree of the vermiform graphite particles and the expansion degree is related to the amount of graphite salts. In our work the factors which can influence the expansion degree in the anodic oxidation method are examined.

Experimental Results and Discussion

2 gm of the Chinese natural graphite (98.4% fixed carbon, -25+50 mesh in particle size) was put in the platinum anode (5 cm in diameter) and covered with glass fibre cloth.

The cathode (5 cm in diameter) was made of artificial graphite and was put above the anode at a distance of 3 cm. Both of the anode and cathode are immersed in 250 ml acidic aqueous solution. The graphite particles after the anodic Oxiation were washed with distilled water until PH=7 and were dried for 1 hr at 60°C. Then they were sent into an electric furnace to expand at the most appropriate temperature.

The final product obtained was the vermiform graphite particles. The density of the original graphite particles D_0 and that of vermiform graphite particles D_V were measured. And we used the ratio of D_0/D_V to express the expansion degree after heating. Evidently the greater the ratio of D_0/D_V, the larger the amount of the forming graphite salts. In our experiments the following factors are examined.

The Concentration of Acid

We used the sulphuric acid aqueous solution of different concentrations (from 18.2 mol/l to 4.55 mol/l). In all the cases, the expansion degree of the vermiform graphite particles was about 400. To compare with the usual immersion oxidation method, the concentration of acid used in the anod-

ic oxidation could be very low. Because under the influence of the external electric field, there are many many intercalation anions (HSO_4^-) around the graphite particles, though the bulk concentration of acid was very low. But it should be noted that the time of anodic oxidation required to reach the same expansion degree of vermiform graphite particles was longer in the dilute acid solition than in the concentrated one. This fact showed that the velocity of forming graphite salts in the dilute solution was slower than in the concentrated one.

We used the nitric acid and perchloric acid to make the similar experiments. The expansion degree of the vermiform graphite particles were above 300.

The Current Density and the Oxidation Time

When the concentration of the acid and the time of oxidation were fixed, the expansion degree of vermiform graphite particles increased with the increase of the current density at the beginning. But when the current density reached a certain value, the expansion degree did not increase again. This current deusity was called critical current density. We found that it was inversely proportional to the oxidation time.

The electric enerty wasted in heat increased with the increase of current density. Therefore it is important to choose an appropriate currert density during anodic oxidation.

The Expansion Degree after Oxidation

The natural graphite particles expanded slightly in the c direction during anodic oxidation. The density of the graphite particles after anodic oxidation D_a was measured and the ratio of D_o/D_a was used to express the expansion degree after oxidation. We found that the expansion degree after heating would decrease when the expansion degree after oxidation was too large (for sulphuric acid solution, over 10-15). It was easy to understand that the large expansion after oxidation would make many leaks from which the gases produced in the decomposition of graphite salts would leak out. Thus the expansion degree after heating decreased.

Conclusion

Using the anodic oxidation method to displace the usual immersion oxidation method, the strong oxidizing agent will not be adopted and the concentration of acid will be very low. These are favourable to safety and the environmental pollution will be prevented.

The controlling factors in the production process are the concentration of acid, the current density, the oxidation time and the expansion degree after oxidation.

Anodic oxidation is an effective method to prepare graphite salts when it is used to produce flexible graphite material. The expansion degree after heating is usually equal to 300-400 times.

References

1. G. R. Hennig, J. Chem. Phys 20 (1952) 1443.
2. M. Inagaki, Carbon 5 (1967) 317
3. U. S. Pat. No. 3,404,061
4. U. S. Pat. No. 4,146,401
5. Jap. Pat. No. 56-18525
6. Jap. Pat. No. 56-90989
7. Jap. Pat. No. 58-161913