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Preparation of Expanded Graphite-based Composites by One Step Impregnation

LIU Chengbao[1], CHEN Zhigang[1*], CHEN Hong[2], MIAO Zhi[2], FU Meng[3]

(1. Department of Chemistry and Bioengineering, Suzhou University of Science and Technology, Suzhou 215009, China;
2. School of Materials Science and Engineering, Jiangsu University, Zhenjiang 212013, China;
3. School of Materials Science and Engineering, Changzhou University, Changzhou 213016, China)

Abstract: A new method for preparing expanded graphite-based composites (EGCs) was developed. The obtained samples were characterized by scanning electron microscopy (SEM), transmission electron microscope (TEM) and nitrogen adsorption. The experimental results indicated that the EGCs was not simply mechanical mixture of EG and activated carbon, instead the activated carbon was coated on the surface of interior and external pores of the EG in the form of thin carbon layer. The thickness of the activated carbon layer was nearly one hundred nanometers by calculation. It was shown that the higher the impregnation ratio and the activation temperature were, the easier the porosity development would be. And the BET surface area and the total pore volume were as high as 1978 m^2/g and 0.9917 cm^3/g respectively at 350 ℃ with an impregnation ratio of 0.9.

Key words: expanded graphite; expanded graphite-based composites; H_3PO_4 activation; pore structure

1 Introduction

Expanded graphite-based composite (EGC) is focussed on because of its many potential applications[1]. Highly compressed EG has been used as seals and gaskets, but the most attractive application for the EG was considered as adsorbent, especially for treatment of industrial waste water[2-5]. The macropores (one to tens of um) and the connectivity of the interior pores give EG nice permeability which is a very important feature for an adsorbent material used in industrial. However, the low BET surface area has impeded its practical application as a high efficient adsorbent material.

The EGCs is a new material that was designed according to following ideas: the EG will be used as the matrix and the activated carbon will be coated on the interior and external pore surfaces. Such materials would not only retain macropores of the matrix with good permeability, but also obtain high surface area. The EGCs were first prepared by J.F. Mareche six years ago[6-8]. After that many authors[9-11] obtained the EGCs using the similar method but different starting materials. So far, because of polymer was selected as carbon source, the procedure was fabricated and difficult to control; and also physical activation method was mainly selected for activation but not chemical activation method, so the highest BET surface area reported was under 1000 m^2/g, much lower than that of the normal activated carbons. In present work, a new kind of EGCs was prepared by one-step impregnation with the sucrose and phosphoric acid as the starting materials. By covering the surface and interior pores of the EG with activated carbon, the expanded graphite and the activated carbon had a good combination. The structure of the EGCs was analyzed and the characterization of the pore size distribution was carried out.

2 Experimental

2.1 Preparation of EGCs

EG was prepared by the method based on a previous work[12]. Sulfuric acid and nitric acid were added into a mixture of natural graphite and $KMnO_4$ at 25 ℃ respectively with stirring. After 30 minutes reaction, the ex-

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LIU Chengbao(刘成宝): Ph D; E-mail: cashbao10_10@163.com

*Corresponding author: CHEN Zhigang(陈志刚): Prof.; E-mail: czg@ujs.edu.cn

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pandable graphite was washed with tap water until the pH value up to 4, and then dried at 80 ℃ until the water content down to 3%. Then the obtained expandable graphite was rapidly put into the furnace at 1000 ℃ for about 10 seconds. The expanded volume was over 350 mL/g.

A certain quantity of EG was immersed into the sucrose–phosphoric acid solution with various concentrations. The impregnation ratio (weight of H_3PO_4 relative to that of sucrose) was varied from 0.3 to 1.2. Then the material was subjected to heat treatment at 80 ℃ in oven for 24 hours and solidified at 150 ℃ for 4 hours. At the end, the material was carbonized and activated in a pipe stove under nitrogen flow for 2 hours. The temperature was controlled between 300 ℃ and 500 ℃. The final product was cooled down to room temperature in the nitrogen atmosphere. The sample was first boiled for several times, and then rinsed with the tap water until no phosphate ions detected by $Pb(NO_3)_4$.

The samples are identified with a C followed by two numbers indicating the impregnation ratio and the activation temperature. Thus, the sample C–0.3–300 corresponds to the EGACs prepared at 0.3 impregnation ratio and 300 ℃ final activation temperature.

2.2 Structure characterization of the EGCs

The phase structure of the Mo modified titanium was analyzed by D/max 2500 X-ray diffraction (XRD) with Cu Kα. The microstructure of the Mo modified titanium was studied on cross sections using Zeiss Axiovert 25CA inverted microscope. The concentration profile of the elements over the thickness of the Mo modified titanium was analyzed using a Spectrum GDS-750A glow-discharge optical emission spectroscope (GDOES).

3 Results and Discussion

3.1 SEM analysis

SEM images (shown in Fig.1) clearly demonstrate the multicomponent structure of the EGCs. On the surface, just partial pores are filled by the activated carbon (Fig.1a). Only a little activated carbon is found in the large spaces among entangled worm-like particles of EG (Fig.1b), while most of the activated carbon is distributed on the surface of the interior pores (Fig.1c and 1d). The thickness of the activated carbon could be calculated according to: $d=m/\rho\times s$, $d=m/\rho\times s$, where S is the surface area of the expanded graphite (40 m^2/g, determined by the BET method), ρ the density of the activated carbon in the EGCs (1.15 g/cm^3, acquired by calculation) and m the mass of the activated carbon in the EGCs (g/g). The thickness of the activated carbon layer that covered the interior and external pores of the EGCs is nearly one hundred nanometers according to above formula. The SEM observation also confirmed this result (see Fig.1d). The distribution of the activated carbon in the EG matrix increased the rigidity of the EGCs while remained the permeability.

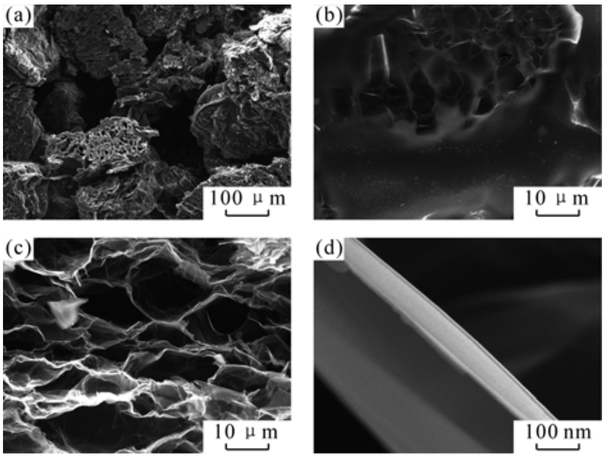

Fig.1 SEM images of surface and interior of EGCs

3.2 TEM analysis

The TEM images of the EGCs are shown in Fig.2. It could be seen that both the external pore surfaces and interior pore surfaces of the EGCs are coated by the activated carbon (Fig.2a). And also the activated carbon is uniformly distributed with a certain thickness (Fig.2b) which is the same result with the SEM analysis.

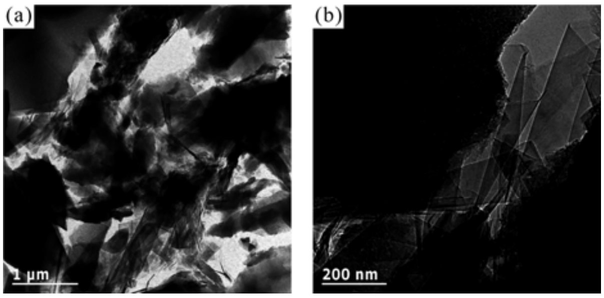

Fig.2 TEM images of EGCs

3.3 Nitrogen adsorption analysis

The adsorption isotherm of the EGCs shown in Fig.3 is typical I-type isotherm, which indicates that the EGCs are mainly composed of micropores[13]. A plateau which is not clearly reached indicated widening of pore widths and a type H4 hysteresis loop in this isotherm exhibites characteristic of slit-shaped pores[14].

The low-pressure hysteresis existed in the isotherm was associated with a distortion of the structure of the EGCs which is difficult to reverse and leads to an increase in the saturation uptake. So the mechanism was an irreversible intercalation within pores of molecular dimensions or the phosphoric acid phase through pre-existing constructions into wider cavities[15, 16].

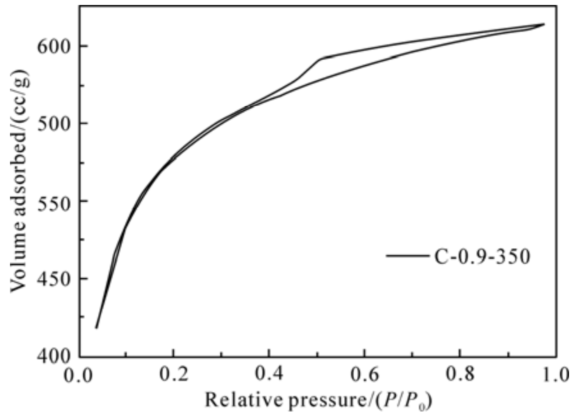

Fig.3 Adsorption isotherm of EGCs by nitrogen adsorption

3.4 The development of pore structure

3.4.1 The effect of impregnation ratio

One of the primary parameters affecting the pore structure of the EGCs made by phosphoric acid activation is the impregnation ratio. The physical structure of the EGCs prepared with different impregnation ratios at 300 ℃ are illustrated in Fig.4.

The results indicated that BET surface area and pore volume of the EGCs reached a maximum at an impregnation ratio of approximately 0.9. Then with the increase of the impregnation ratio, the portion of micropore volume decreased while mesopore volume increased rapidly.

It is generally accepted that the porosity is generated by intense washing to eliminate the phosphoric acid remaining in the internal structure of the EGCs[17]. And it was found by Molina-Sabio[18] that there was a good agreement between the volume of micropores and the volume occupied by the acid phase existed after the activation. So with the initial increase of impregnation ratio before 0.9, the reaction was engaged in pore generation, so the BET surface area, total pore volume and micropore volume of EGCs increased, and reached a maximum at the impregnation ratio of 0.9.

The formation of mesopores has been attributed to the pore widening or even the collapse of micropore walls[19]. So as impregnation ratio continued to increase, more phosphoric acid is incorporated into skeleton of precursor, and localized reactions become increasingly more significant[20]. Species such as H_3PO_4, $H_4P_2O_7$, $H_5P_3O_{10}$ and some others in lower concentrations (*eg*, $H_{n+2}P_nO_{3n+1}$)[21], each one with a different molecular size were present in the above mentioned mixture. This caused more mesopore generating while less micropore increased, so the BET surface area and the portion of micropore volume decreased while mesopore volume increased rapidly.

3.4.2 The effect of activation temperature

The BET surface area and porosity do not develop at the temperature lower than 300 ℃, thus only characterization results of the EGCs prepared at the activation temperature higher than 300 ℃ are displayed in Fig.5.

As could be seen, activation proceeded at relatively low temperature, giving rise to a considerable development of BET surface area and pore volume. At an impregnation ratio of 0.9, the BET surface area and the total pore volume reached a maximum value close to 2000 m^2/g and 1 cm^3/g respectively at around 350 ℃ and then decreased rapidly. The portion of micropore volume decreased while mesopore volume increased slowly.

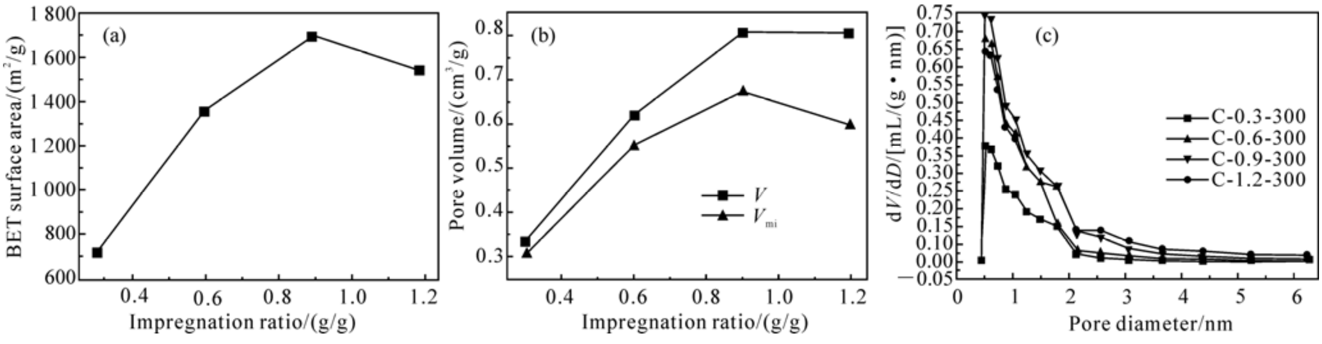

Fig.4 Effect of impregnation ratio on (a) BET, (b) pore volumes and (c) pore distribution of EGCs by H_3PO_4 activation at a final activation temperature of 300 ℃

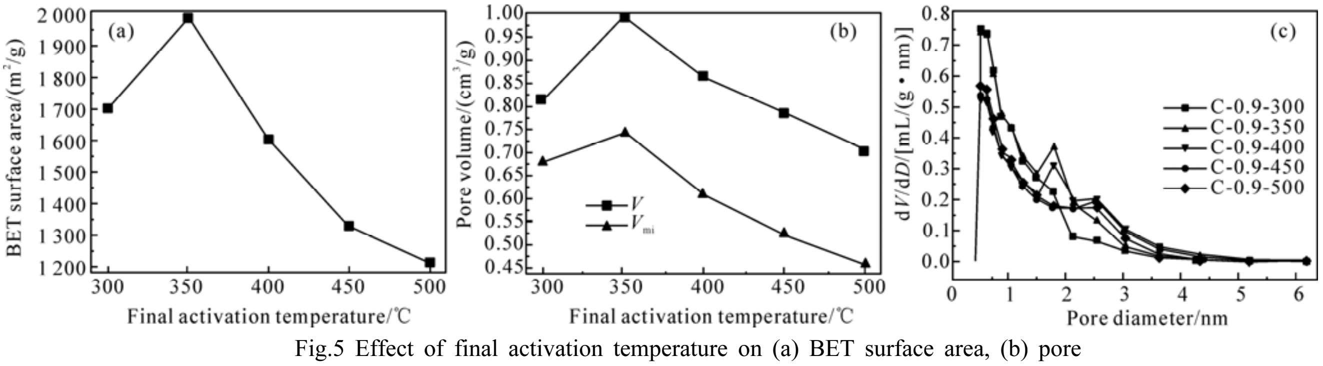

Fig.5 Effect of final activation temperature on (a) BET surface area, (b) pore volumes and (c) pore distribution of EGCs at an impregnation ratio of 0.9

The BET surface area and micropore volume of the EGCs increased with the initial increasing of the final activation temperature probably because of increased interaction between phosphoric acid and sucrose, and more intensive pyrolysis of starting materials. With an initial increase of activation temperature below 350 ℃, the activation rate tends to be faster and more micropores were generated, so the BET surface area and pore volume increased and reached a maximum value at around 350 ℃. And then, with the continued increase of the temperature, the widening of micropores was gradually reinforced, so more mesopores were generated. And also with the increase of the temperature, more phosphoric acid which inhibits the collapse of pore walls[22] were gasified. The reasons above resulted for the decrease of the BET surface area and the micropore volume while the increase of the mesopore volume.

4 Conclusion

A new method for preparing a new kind of EGCs from expanded graphite, activated carbon was proposed. The EGCs was not just the mixture of the EG and the activated carbon, but instead the activated carbon was coated on the surface of interior and external pores of the EG in the form of thin carbon layer. The thickness of the activated carbon layer was nearly one hundred nanometers by calculation. The results indicated that the more impregnation ratio and final activation temperature, the easier the porosity developed, especially the mesoporosity. The interaction between incorporated activation reagent and the surrounding precursor was the primary factor responsible for the porosity evolution, especially the micropores. The formation of mesopores was attributed to the widening of pore widths or even the collapse of micropore walls.

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