SYNTHESIS OF GRAPHITE INTERCALATION COMPOUNDS WITH LOW SULFUR CONTENT

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Introduction

Residue compounds with sulfuric and nitric acids are conventionally used in industrial production of flexible graphite. However, there are at least two major disadvantages associated with this process. First, the intercalation and exfoliation processes cause environmental pollution as they release large amounts of toxic gases SO_x and NO_y. Second, the residue acids in the flexible graphite are corrosive during service [1]. The amount of corrosive residuals in flexible graphite can be critical, particularly for application in nuclear power plants, electronics, aerospace and automobile industries.

Considerable efforts have been made to produce totally sulfur-free flexible graphite or at least to reduce the sulfur content in exfoliated GICs. In the present work, hydrogen peroxide as a moderation oxidizing agent is used, exfoliated graphite with relatively low sulfur content is synthesized. In addition, synthesis of H_2SO_4-GICs in diluting H_2SO_4 by an electrochemical method is performed, in which sulfuric acid is partially replaced by acetic acid. Finally, sulfuric acid is entirely replaced with some organic acids which are no pollution and corrosion at all.

Experimental

100g natural graphite with 99.9 wt% carbon content and 0.3mm average flake size, 100ml 98 wt% H_2SO_4, hydrogen peroxide with different concentration (from 30 to 60 wt%) and volume was used each process. Graphite was poured into the mixture of H_2SO_4 and H_2O_2, and blended each other, reaction was lasted 60 min. at room temperature, then the reacted graphite was washed with water until its pH value attaining 6~7, then dried at 120°C for 4 hrs. The obtained residue GIC was exfoliated in Muffle furnace at 1000°C for 10 sec, the exfoliation volume was measured by a graduated cylinder, and its residue sulfur content was measured by a SC analyzer.

About 0.1g natural graphite was used as working electrode. All electrochemical measurements were carried out using computerized potentiostat (EG&G 273). A 100 ml electrolyte solution was used in each synthesis process. H_2SO_4-GIC is synthesized in pure H_2SO_4, H_2SO_4-CH_3COOH. HCOOH-GIC is synthesized in pure formic acid. Chronopotentiomerty (CE) was adopted to synthesize GICs at different applied anodic current density varied from 0.1 to 20 mA/cm^2.

Results and Discussion

1. Low sulfur GIC synthesized in H_2SO_4-H_2O_2

Hydrogen peroxide (H_2O_2) has been used to replace the strong oxidizing agents for the intercalation of H_2SO_4 into graphite owing to its mild nature, low cost and environmental friendliness [2]. Among the factors that affect residue sulfur content and exfoliation volume of GICs, concentration of H_2O_2 and ratio of H_2SO_4/H_2O_2 are two of the most important. Figure 1 shows that sulfur content and exfoliation volume increases as the concentration increases. As the concentration of H_2O_2 increase, the oxidation capability of the solution becomes strong, it results in intercalation much easy, and intercalate amount in the graphite layer increases, thus, both exfoliation volume and residue sulfur content are high.

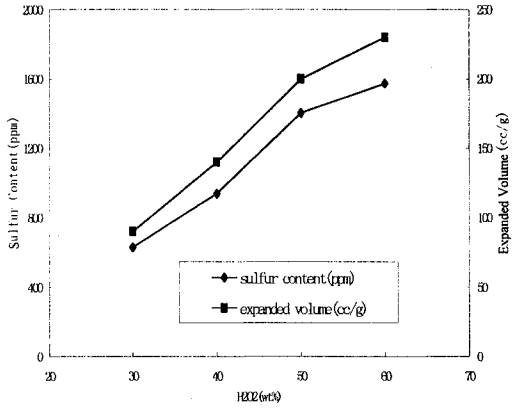

Figure 1 The Correlation between concentration of H_2O_2 and sulfur content & expanded volume.

2. Low-sulfur GICs synthesized in diluting H_2SO_4

Sulfur contents of the GICs synthesized in the electrolyte of 50 vol.% H_2SO_4-CH_3COOH were examined before and after exfoliation and tabulated in Table 1 [3]. For comparison, Table 1 also lists the sulfur contents for GICs synthesized in 18 *M* H_2SO_4. The sulfur content of the samples synthesized in diluted sulfuric acid is much lower than that synthesized in high concentration sulfuric acid under each stage number before exfoliation. This fact suggests that acetic acid may partially replace some sulfuric acid during the formation of bisulfate GICs.

3.Sulfur-free GIC synthesized in organic acids

Formic acid-GIC with stage 3 to 5 structures are electrochemically synthesized wherein formic acid serves as both the electrolyte and the intercalate source. The synthesized compounds exhibit excellent exfoliation ability, their expansion volume reach 100-300 ml/g at the temperature range of 400-800 °C [4]. Such organic GICs do not contain any corrosive species. Other organic acids with relative high acidity, glyoxylic acid and oxalic acid, may be used for electrochemical synthesis of GICs.

Conclusions

1.For chemical synthesis of H_2SO_4-GIC, in which H_2O_2 was used as an oxidant, concentration of H_2O_2 and ratio of H_2SO_4/H_2O_2 have important influences on residue sulfur content and exfoliation volume of GICs.

2.GICs with lower or non sulfur contents can be synthesized using the electrochemical method by means of partially replacing H_2SO_4 with co-intercalation of organic acid, or totally replacing with organic acid-GICs.

Acknowledgements

We are grateful for the financial support from the National Science Foundation Committee of China under Grant No. 59872017.

References

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Table 1 Sulfur content of the synthesized compounds in different electrolyte before and after exfoliation

Stage No of	Synthesized in 18 *M* H_2SO_4		Synthesized in 50 vol CH_3COOH+50 vol% H_2SO_4	
Synthesized Sample	Before exfoliation	After exfoliation	Before exfoliation	After exfoliation
1	10.2 wt%	2500 ppm	6.2 wt%	800 ppm
2	6.1 wt%	1500 ppm	4.5 wt%	500 ppm
3	4.7 wt%	1100 ppm	3.6 wt%	400 ppm