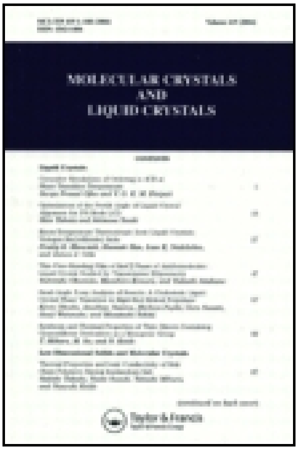

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Synthesis, Structure and Electrochemical Reactivity of CrO_3-H_2SO_4- Graphite Bi-Intercalation Compounds Prepared at Room Temperature

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The paper deals with the synthesis, structure and electrochemical properties of CrO_3-H_2SO_4-graphite bi-intercalation compound (CrO_3-H_2SO_4-GBC) prepared at room temperature. In contrast to the two step process in which CrO_3 is first intercalated chemically followed by electrochemical bi-intercalation of H_2SO_4, the method described in the paper allows the simultaneous intercalation of CrO_3 and H_2SO_4 into graphite to give CrO_3-H_2SO_4-GBC. The electrochemical method appeared to be suitable both to distinguish the original CrO_3-H_2SO_4-GBCs of different structures and to enrich them with H_2SO_4 to provide stage-1 compound.

Keywords: graphite bi-intercalation compounds; CrO_3; H_2SO_4; XRD; EDX

INTRODUCTION

The depth of intercalation for CrO_3 in CrO_3-graphite intercalation compounds (CrO_3-GICs) prepared in hot glacial acetic acid is limited to about 30 µm[1-4] Because of this, only the peripheral regions of large flakes of graphite as well as the HOPG slabs are intercalated with CrO_3 whereas the graphite core remains free of intercalate. Until now, the formation of CrO_3-H_2SO_4-graphite bi-intercalation compound (CrO_3-H_2SO_4-GBC) has been shown to take place upon the subsequent anodic intercalation of H_2SO_4 into the primary stage ($n \geq 2$)-CrO_3-GIC[2,3,5,6]. The present paper provides the results showing that ternary graphite bi-intercalation compounds with CrO_3 and H_2SO_4 (CrO_3-H_2SO_4-GBCs) can directly be prepared at room temperature.

EXPERIMENTAL

Stage-7 CrO_3-H_2SO_4-GBC (C/Cr=48.4; Cr/S=3.9) was prepared on soaking the flaky graphite (99.9 wt% C; Graphitwerk Kropfmühl) in the solution of CrO_3 in glacial CH_3COOH admixed with 0.2 M H_2SO_4 for 8 days (sample 1), whereas stage-6 CrO_3-H_2SO_4-GBC (C/Cr=42.2; Cr/S=15.6) was prepared for 35 days (sample 2). For comparison, stage-6 CrO_3-GIC containing the phase of unreacted graphite (C/Cr = 44.6) was synthesized in CrO_3/CH_3COOH solution at 120 °C (sample 3) according to the procedure described earlier [3,5,7]. The X-ray diffraction (XRD) measurements were performed using Cu Kα radiation. For observing the concentration profiles of intercalates in CrO_3-H_2SO_4-GBCs the energy dispersive X-ray (EDX) analysis coupled with scanning electron microscopy (SEM) was used. The subsequent intercalation/deintercalation of H_2SO_4 into GBCs was carried out in 18 M H_2SO_4 by the cyclic woltammetry (CV) using the reference Hg/Hg_2SO_4/1M H_2SO_4 electrode.

RESULTS AND DISCUSSION

The XRD pattern recorded for sample 1 (Fig. 1a) exhibits a set of intercalation peaks corresponding to stage-7 structure. A small shoulder observed on the main 7(008) peak can be related to the (002) graphite peak indicating the presence of pure graphite in CrO_3-H_2SO_4-GBC. However, because some intercalate is inevitably expelled from the edge regions of flakes of CrO_3-H_2SO_4-GBC due to the washing with CH_3COOH and acetone, a slight amount of pure graphite in the compound can be ascribed to the purification treatment. In the light of this, it can be assumed that in the course of intercalation the whole interlayer spacing of graphite is filled with intercalate.

A strong corroboration of this assumption is given by the EDX data (Fig. 2). The distribution profiles for S and Cr show that both intercalates, CrO_3 and

H_2SO_4, are present in the whole area of the flake but markedly less CrO_3 is accumulated at the flake centre. It means that 8 days of intercalation is long enough for CrO_3 to reach the centre of graphite flake. The profiles are complementary suggesting the existence of the CrO_3-H_2SO_4 co-intercalation domains in which the zones of accomodation of CrO_3 and H_2SO_4 are distinguished. As seen from Fig. 3, the distribution profiles for both intercalates changed noticeably after the following 27 days of intercalation giving almost flat lines with only small peaks arising from the island-like arrangement of intercalates. In comparison with sample 1, chemical analysis of sample 2 exhibited higher amount of chromium and lower amount of sulphur. Based on this, it is reasonable to assume that on continuing the process of intercalation more and more CrO_3 penetrated the inner regions of co-intercalation layers resulting in the displacement of H_2SO_4 intercalate. This process could lead to the removal of H_2SO_4 from the co-intercalation layer to leave the graphite lattice or to move in the adjacent graphite galleries free of

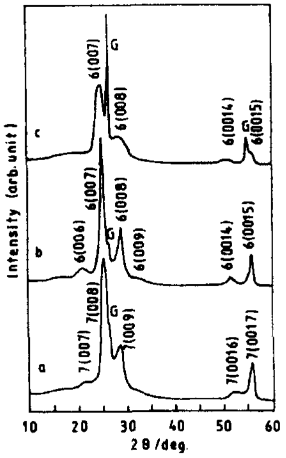
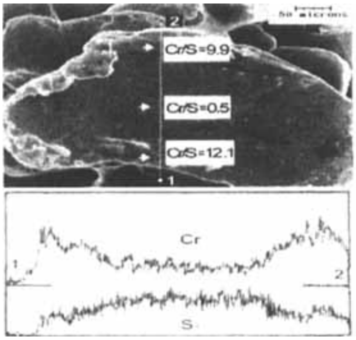


FIGURE 1 XRD patterns of (a) stage-7 CrO_3-H_2SO_4-GBC (sample 1), (b) stage-6 CrO_3-H_2SO_4-GBC (sample 2), (c) stage-6 CrO_3-GIC (sample 3). Cu Kα radiation

CrO_3. The latter case is more probable due to a very high concentration of CrO_3 oxidizer in the CrO_3/H_2SO_4 solution used for intercalation. In such a case, the decrease in the stage number of GBC as well as the diminution of H_2SO_4 in the co-intercalation domains should take place. The proposed mechanism of intercalation is consitent with the XRD data which showed that stage-7 CrO_3-H_2SO_4-GBC (sample 1) (Fig. 1a) changed with time to stage-6 compound (sample 2) (Fig. 1b). By comparison, the product of intercalation obtained at elevated temperature in CrO_3-CH_3COOH solution free of H_2SO_4 (sample 3) is composed of stage-6 CrO_3-GIC and a large amount of unreacted graphite (Fig. 1c). The EDX results recorded for this product (not presented here) are identical to those published previously for CrO_3-GIC prepared in hot CrO_3/CH_3COOH solution[1-3], i.e., chromium is intercalated only at the peripheral zones of the graphite flake.



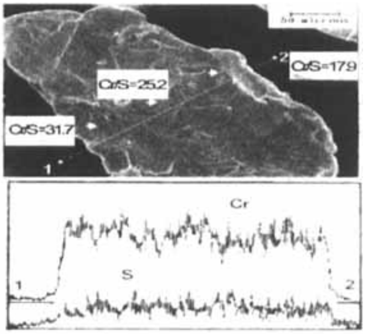


FIGURE 2 SEM micrograph and EDX distribution curves for chromium and sulphur of the flake of stage-7 CrO_3-H_2SO_4-GBC (sample 1).

FIGURE 3 SEM micrograph and EDX distribution curves for chromium and sulphur of the flake of stage-6 CrO_3-H_2SO_4-GBC (sample 2).

The differences in the structure and composition of GBCs are reflected on the CV curves in 18 M H_2SO_4 which illustrate the process of the subsequent electrochemical intercalation/deintercalation of H_2SO_4 (Fig. 4). A characteristic feature of this process are the cathodic leaps appearing on both curves during the forward bi-intercalation scan. According to the mechanism reported previously for bi-intercalation of H_2SO_4 into CrO_3-GIC[2,3,5], this effect takes place when all the graphite galleries free of CrO_3 in CrO_3-GIC are wholly occupied with the secondary H_2SO_4 intercalate (stage-1 CrO_3-H_2SO_4-GBC), and on increasing the potential of electrode H_2SO_4 invades the graphite galleries filled with CrO_3. As a consequence, the CrO_3-H_2SO_4 co-intercalation layers form within CrO_3-H_2SO_4-GBC and some CrO_3 is simultaneously expelled from the graphite lattice. From comparison of Figs. 4a and 4b, it is seen that the single cathodic peak for sample 1, with a small shoulder at 0.92 V, is smaller in charge (- 4.4 C) as compared to the quadruple peak (-7.2 C) for sample 2 composed of very sharp leaps. The CV characteristics observed for both GBCs can be interpreted in terms of the differences in the structure and composition. The observation that the curves are similar in character until the anodic peak at 0.74 V is completed (the formation of stage-1 structure), indicates that for both compounds H_2SO_4 occupies first the graphite galleries free of intercalate and then is forced by increasing potential (controlled by a voltage generator) to move in the galleries filled with the primary intercalates, CrO_3 and H_2SO_4. A lower potential at which the cathodic leap starts to begin means that the removal of CrO_3 from CrO_3-H_2SO_4-GBC by

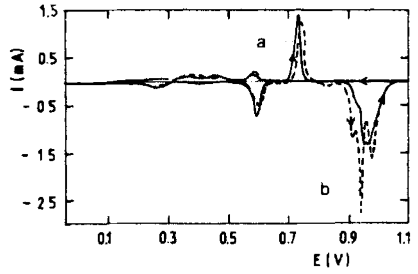


FIGURE 4 Cyclic voltammograms recorded during the subsequent intercalation/deintercalation of 18 M H_2SO_4 for (a) (—) stage-7 CrO_3-H_2SO_4-GBC (sample 1) and (b) (– –) stage-6 CrO_3-H_2SO_4-GBC (sample 2). Scan rate: 0.02 mV/s, electrode mass: 20 mg.

the co-intercalating H_2SO_4 is easier. According to this, CrO_3 is easier deintercalated from sample 2 than from sample 1. A lower resistance of sample 2 to deintercalation might be attributed to a denser arrangement of intercalates as well as more pronounced repulsion between CrO_3 and HSO_4 ions in the co-intercalation domains as the electrochemical invasion of H_2SO_4 occurs. The charge involved in the cathodic peaks is higher for sample 2 which can simply be ascribed to higher amount of CrO_3 whereas the multiple cathodic leaps recorded on the CV curve suggest that the CrO_3 islands of different energy bonding exist in co-intercalation domains[3]. Because CrO_3 is not deintercalated from CrO_3-H_2SO_4-GBC due to the cathodic reduction[3,6], somewhat smaller charge noted for sample 2 during the backward scan can be related to lower amount of H_2SO_4 removed from GBC.

Acknowledgements
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