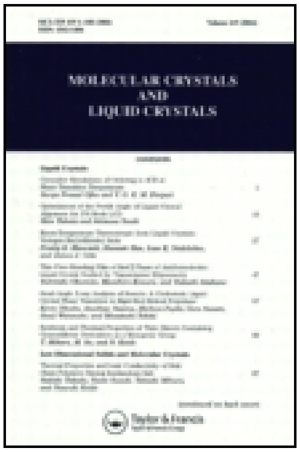

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Effect of Polyaniline on Electrochemical Intercalation of Sulphuric Acid into CrO_3-Graphite Intercalation Compound

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Effect of Polyaniline on Electrochemical Intercalation of Sulphuric Acid into CrO_3-Graphite Intercalation Compound

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Abstract The influence of the oxidation reactions of aniline on the process of the subsequent intercalation of H_2SO_4 into CrO_3-GIC is examined. It is shown that due to the polymerization of aniline the pristine CrO_3-GIC is protected against deintercalation in 6 M H_2SO_4 and the anodic charge noted in the potential range of bi-intercalation increases significantly. From the results obtained it can be inferred that the products of polyaniline oxidation are involved in bi-intercalation reactions.

Keywords: electrochemical bi-intercalation; graphite; CrO_3; H_2SO_4; polyaniline.

INTRODUCTION

CrO_3-H_2SO_4-graphite bi-intercalation compounds (CrO_3-H_2SO_4-GBCs) are formed upon the subsequent anodic intercalation of H_2SO_4 into the host graphite intercalation compounds with CrO_3 (CrO_3-GICs). In contrast to stable CrO_3-H_2SO_4-GBCs prepared in 18 M H_2SO_4[1-3], a large amount of CrO_3 is irretrievably deintercalated from the host CrO_3-GIC on the successive electrochemical intercalation in 12 M H_2SO_4[4,5]. The depletion of a marked amount of the CrO_3 intercalate from the edge regions of CrO_3-GIC due to hydrolysis occurs already before the potential scanning is started. On decreasing the concentration of H_2SO_4 deintercalation of CrO_3 occurs more and more violently.

Recently it has been found that the bi-intercalation process changes for the better if aniline is added to 9 M H_2SO_4[6].

The aim of the present paper is to examine the influence of aniline oxidation on the mechansim of bi-intercalation of H_2SO_4 into CrO_3-GIC occurring in 6 M H_2SO_4. The interaction between the original CrO_3-GIC and the polyaniline (PANI) film as well as the products of its oxidation are considered to explain an enhanced stability of CrO_3-H_2SO_4-GBC.

EXPERIMENTAL

CrO_3-GIC was prepared on refluxing the graphite flakes in a glacial acetic acid/CrO_3 solution according to the procedure described previously[7,8]. X-ray diffraction (XRD) analysis showed the intercalation product to be stage-3 CrO_3-GIC (I_c = 1.458 nm, C/Cr = 24.0) admixed with the phase of the pristine graphite. Electrochemical intercalation of H_2SO_4 into both the pristine graphite and the CrO_3-GIC was performed in pure 6 M H_2SO_4 as well as in 0.02 M solution of aniline in 6 M H_2SO_4. All electrochemical measurements were performed using a computer-controlled EG&G Model 273A potentiostat/galvanostat. The working electrode was examined in the form of a particle bed (100 mg)[4,8]. The counter electrode was a platinum wire, whereas the reference electrode was Hg/Hg_2SO_4/1 M H_2SO_4 (0.674 V vs. SHE) connected to the solution under investigation by a Luggin capillary. All potentials, E, quoted in this paper were measured against this electrode. The potential scanning (at v = 0.1 mV/s) was performed in the potential range from - 0.6 to 1.05 V, starting from the rest potential of the electrode (after 0.5 h of the open circuit equilibration) to the positive direction. Galvanostatic measurements were carried out at the current density of 1.0 mA/g. All the experiments were carried out at 20 °C.

RESULTS AND DISCUSSION

The voltammetric curves recorded for graphite are depicted in Figure 1. Curve *a* represents intercalation of graphite occurring in 6 M H_2SO_4. As seen from this curve, the formation of high-stage H_2SO_4-GIC starts at the high potential of 0.97 V but instead of a well shaped anodic peak a steep increase in current

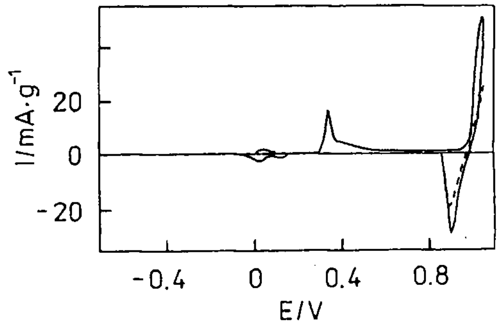


FIGURE 1 Voltammograms recorded for the pristine graphite in (a) 6 M H_2SO_4 (– –) and in (b) 6 M H_2SO_4 + 0.02 M aniline (—).

is only observed. The charge arising from deintercalation of H_2SO_4 is involved in cathodic peak at 0.9 V after the potential scanning is reversed. The presence of 0.02 M aniline in the acidic solution (Fig. 1b) effects in a double anodic peak (from 0.3 to 0.55 V) associated with the polymerization reactions occurring at the graphite surface. Diradical dications generated at such high potentials were reported to force further polymerization in the presence of aniline in the electrolyte, or to contribute to a degeneration reaction (via hydrolysis) when there is no aniline[9]. As seen from curve *b*, PANI exerts an influence on the intercalation of H_2SO_4 into the graphite host. The reaction develops within a defined peak, the charge of which is over twice that noted in pure H_2SO_4.

As expected, the formation of CrO_3-H_2SO_4-GBC in 6 M H_2SO_4 is ineffective because of the competitive reactions of deintercalation bringing about the decomposition of both CrO_3-GIC and CrO_3-H_2SO_4-GBC (Fig. 2a). Deintercalation of CrO_3-GIC occurs immediately after pouring the electrode with H_2SO_4 solution. As the eruption of a large amount of CrO_3 from the graphite lattice to the solution takes place, the potential of the electrode raises rapidly and stabilizes at over 0.7 V. The maximum current of bi-intercalation noted at 1.05 V is very small due to hydrolysis affecting CrO_3-H_2SO_4-GBC. A very broad cathodic peak recorded during the backward sweep is related to the reduction of deintercalated Cr(VI) ions present in the solution[10]. This peak develops in a wide range of potentials suggesting a progressive deintercalation.

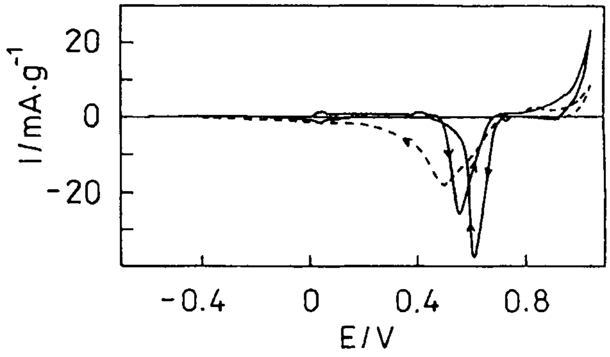
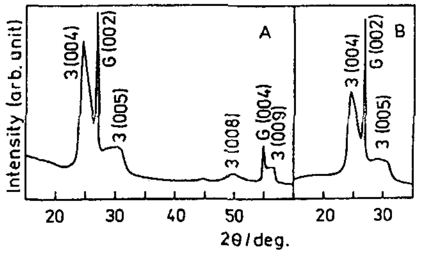


FIGURE 2 Voltammograms recorded for stage-3 CrO_3-GIC in (a) 6 M H_2SO_4 (– –) and in (b) 6 M H_2SO_4 + 0.02 M aniline (—).

The subsequent intercalation of H_2SO_4 into CrO_3-GIC occurs in a different way if aniline is present in the electrolyte. The most striking effect in Fig. 2b is the abrupt cathodic jump beginning at about 0.5 V during the forward scan. To account for the origin of this effect the following mechanism of the process is presumed. The shift of the rest potential from 0.72 V on the immersion of the CrO_3-GIC electrode in the electrolyte to 0.35 V after 0.5 h of the equlibration time, i.e. to the position of the polymerization peak in Fig. 1b, is indicative of the chemical polymerization of aniline on the graphite flake surface occurring at the high potential fixed by CrO_3 appearing in the electrolyte due to deintercalation of CrO_3-GIC. The protective function of PANI film was evidenced in the following experiment. CrO_3-GIC was soaked in solution of 0.1 M aniline in 6 M H_2SO_4 for 30 days, then filtered and exposed to air for 7 days at ambient temperature. The XRD patterns depicted in Fig. 3 show that the staging structure of CrO_3-GIC is not affected by the electrolyte. The increase in the intensity of the graphite peaks as compared to the intensity of the intercalation peaks resulted from some deintercalation of CrO_3 which, in turn, promoted the polymerization reaction of aniline. It is worth noting here that CrO_3-GIC appeared to be unstable in a blank H_2SO_4 (XRD pattern not presented here). Deintercalation of CrO_3-GIC stops as PANI film becomes sufficiently dense and impermeable to water. The process of polymerization is going on as the potential increases. A small and constant current recorded



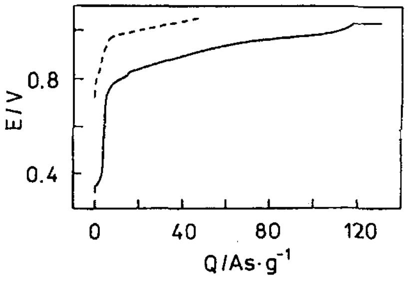


FIGURE 3 XRD patterns recorded for (a) the original stage-3 CrO_3-GIC and for (b) stage-3 CrO_3-GIC after 30 days of immersion in 6 M H_2SO_4 + 0.1 M aniline followed by exposure to air for 7 days. CuKα radiation.

FIGURE 4 Galvanostatic curves recorded for stage-3 CrO_3-GIC in (a) 6 M H_2SO_4 (– –), and in (b) 6 M H_2SO_4 + 0.02 M aniline (—).

before the cathodic jump appears in Fig. 2b, is related to the increase in a double-layer capacitance at PANI/solution interface[11]. Because HSO_4^- ions are specifically adsorbed at the electrode surface[12], on increasing the electrode potential their concentration in the chemically formed PANI/solution interface increases which, in turn, makes electropolymerization easier. However, PANI film may be deteriorated upon the formation of diradical dications as the concentration of monomer is insufficient[9,13]. The concentration of aniline in the vicinity of the electrode decreases due to a partial consumption occurring during precedent chemical polymerization. When an extremely high potential is imposed on the electrode it is likely that the transformation from a tight to a porous structure of the overoxidized PANI film occurs. In such a case, the CrO_3 intercalate, residing at the peripheral regions of the graphite flakes, can easily diffuse through the PANI film to the solution and, in consequence, the potential of the electrode rises abruptly. Because the potential fixed at this moment exceeds the potential imposed on the electrode by the potentiostat, a resulting cathodic current is recorded (Fig. 2b). After the current returns to the positive current side, the increased charge is noted on the voltammogram in the potential range of intercalation. This observation agrees with the results illustrated in Fig. 4. Owing to aniline present in

H_2SO_4 an almost three times larger charge is integrated up to 1.05 V. The overoxidation of PANI does not seem to be the only reason for the increase in charge. The presence of the cathodic peak recorded on the voltammogram at 0.6 V during the backward run (Fig. 2b) is tentatively attributed to the reduction of counter-chromate ions incorporated in the PANI structure together with HSO_4^- ions or/and residing at the graphite/PANI interface. This peak, in contrast to that arising from the reduction of deintercalated chromates (Fig. 2a), is narrow, positively shifted and reproducible on cycling. Based on this, it may be assumed that partly damaged PANI film still plays the role of protective membrane but with specific properties. The counter-HSO_4^- ions incorporated in the polymer are effectively transferred to the CrO_3-GIC lattice contributing to the formation of CrO_3-H_2SO_4-GBC whereas the process of deintercalation is blocked. A corollary to this view is the lack of deintercalation peak in Fig. 2b.

Acknowledgements

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