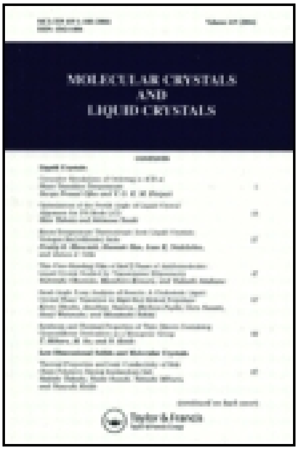

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$ZnCl_2$-CrO_3-H_2SO_4-Graphite Bi-Intercalation Compound: Synthesis, Structure and Electrochemical Transformation

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$ZnCl_2$-CrO_3-H_2SO_4-Graphite Bi-Intercalation Compound: Synthesis, Structure and Electrochemical Transformation

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The paper deals with the synthesis of $ZnCl_2$-CrO_3-H_2SO_4-graphite bi-intercalation compound ($ZnCl_2$-CrO_3-H_2SO_4-GBC). For observing the concentration profiles of intercalates in both $ZnCl_2$-GIC and $ZnCl_2$-CrO_3-GBC the energy dispersive X-ray (EDX) analysis coupled with the scanning electron microscopy (SEM) were used. The X-ray diffraction (XRD) analysis and the cyclic voltammetric (CV) measurements were used to investigate the transformation of the starting $ZnCl_2$-GIC to the ternary $ZnCl_2$-CrO_3-GIC followed by the successive electrochemical intercalation of H_2SO_4 resulting in the quaternary $ZnCl_2$-CrO_3-H_2SO_4-GBC. The present results argue for the formation of co-intercalation domains embedded in the lattice of bi-intercalation compound.

Keywords: graphite bi-intercalation compound; $ZnCl_2$; CrO_3; H_2SO_4

INTRODUCTION

$ZnCl_2$-graphite intercalation compound ($ZnCl_2$-GIC) is easily obtained by the vapour-phase reaction[1]. $ZnCl_2$-GIC was also prepared electrochemically in aqueous solution of $ZnCl_2$ during the galvanostatic and potentiostatic oxidation of graphite[2]. Recently, a potentiodynamic method was used to form $ZnCl_2$-GIC[3]. Graphite bi-intercalation compounds (GBCs) are formed when the vacant interlayer spacings of graphite in graphite intercalation compounds (GICs) with the stage number $n \geq 2$ are successively filled with another intercalate. Recently, GBCs have attracted considerable attention because of their novel properties arising from a variety of fascinating structures and compositions[4]. GBCs involving metal oxides are not numerous. Among them are those with CrO_3 and transition metal chloride (e.g. $FeCl_3$-CrO_3-GIC[5], $ZnCl_2$-CrO_3-GBC[3]) as well as with Brønsted acids[6-9].

EXPERIMENTAL

$ZnCl_2$ was intercalated into natural graphite (Graphitwerk Kropfmühl AG, Germany) from 12 M aqueous solution. The process was carried out by galvanostatic method at 80 °C rising the current density of 6.0 mA/g. $ZnCl_2$-GIC washed out with acetone and dried was then used as the host matrix in the reaction with CrO_3. Intercalation was carried out in the solution of CrO_3 in glacial CH_3COOH at 80 °C for 3.5 h according to the procedure described elsewhere[6,10]. The product of intercalation was successively intercalated with 18 M H_2SO_4 using the voltammetric method (scan rate 0.02 mV/s, the Hg/Hg_2SO_4/1 M H_2SO_4 as the reference electrode). Starting at the rest potential of electrode the intercalation process was continued up 1.1 V. Then the potential of electrode was automatically decreased down to - 0.05 V to observe the process of deintercalation. For characterisation of the structure of GICs the XRD measurements were performed using CuKα radiation. For observing the concentration profiles of intercalates in $ZnCl_2$-GIC and $ZnCl_2$-CrO_3-GBC the EDX method was combined with a scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

As seen from the X-ray diffraction (XRD) pattern illustrated in Fig. 1a, the host stage-5 $ZnCl_2$-GIC (I_c = 2.30 nm) is admixed with the phase of unreacted graphite. The EDX profiles for Zn and Cl (Fig. 2) show that $ZnCl_2$ is nearly uniformly distributed in the whole flake. However, the intensity peaks on the distribution lines demonstrate the island-like arrangement of intercalates. The XRD pattern obtained after the subsequent intercalation of CrO_3 into $ZnCl_2$-GIC is displayed in Fig. 1b. From this pattern it is calculated that the product of the successive intercalation is built up of domains of stage-6 $ZnCl_2$-GIC (I_c = 2.63 nm) and stage-6 CrO_3-GIC (I_c = 2.47 nm). Figure 3 shows the distribution profiles for Zn, Cl and Cr. On inspecting the profiles for Zn and Cl it is clear that near the flake edges the concentration of intercalate is markedly diminished. This fact can be ascribed to dissolving some $ZnCl_2$ from the peripheral regions of the graphite both upon the successive intercalation of CrO_3 in CH_3COOH solvent and due to the washing of the product of bi-intercalation with the acid. The other difference, as compared to the profiles shown in Fig. 2, is that the intensity peaks for Zn and Cl are larger and separated with deep gaps. A very interesting feature observed in Fig. 3 is that the profiles corresponding to the arrangement of Zn, Cl and Cr in the graphite flake are complementary; a higher concentration of $ZnCl_2$ a lower concentration of CrO_3. It suggests that during the subsequent intercalation of CrO_3 into the host $ZnCl_2$-GIC the secondary intercalate invades the graphite galleries occupied with the primary intercalate resulting in the rearrangement of $ZnCl_2$ and a partial removal of this intercalate from the graphite lattice to the solution. The latter phenomenon is supported by the fact that the stage number of GIC changes from 5 to 6 after the successive intercalation of CrO_3. The observation of the dislocation of basal planes observed at the centre of the graphite flake (Fig. 3) allow to infer that the ingress of CrO_3 into $ZnCl_2$-GIC occurred both through the flake edges and the crystalline boundaries. In the light of the fact that in the experimental conditions used in this work CrO_3 is capable of intercalating the pure graphite, it is reasonable to assume that upon the subsequent intercalation of CrO_3 into the host $ZnCl_2$-GIC the co-intercalation domains are formed within the bi-intercalation compound in a

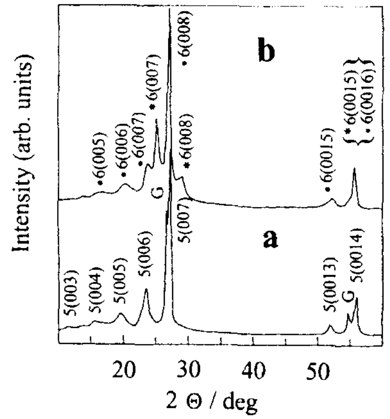

FIGURE 1 X-ray diffractogram of $ZnCl_2$-GIC (a), $ZnCl_2$-CrO_3-GBC (b)
* stage-6 CrO_3-GIC, • stage-6 $ZnCl_2$-GIC.

similar way as for CrO_3-H_2SO_4-GBC, CrO_3-$HClO_4$-GBC[9] and $FeCl_3$-CrO_3-GBC[5].

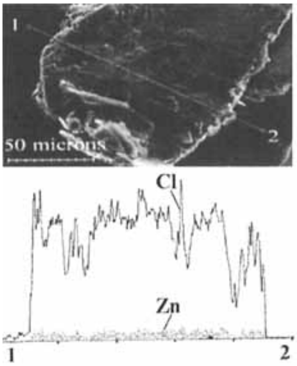

FIGURE 2 SEM micrograph and EDX distribution curves for zinc and chlorine of the flake $ZnCl_2$-GIC.

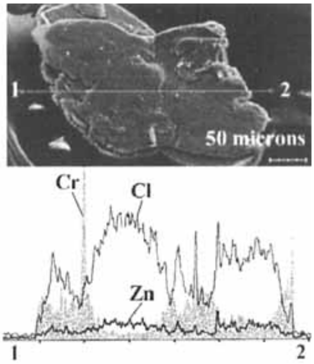

FIGURE 3 SEM micrograph and EDX distribution curves for zinc, chromium and chlorine of the flake $ZnCl_2$-CrO_3-GBC.

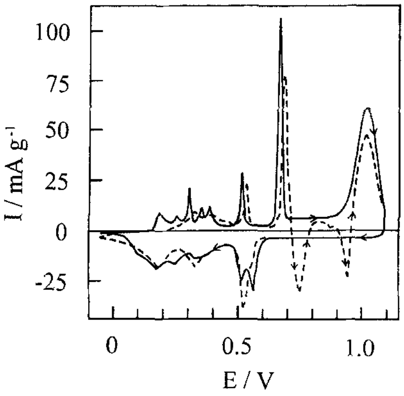

FIGURE 4 CV curves recorded during intercalation/deintercalation of 18 M H_2SO_4 into (a) $ZnCl_2$-GIC (——), (b) $ZnCl_2$-CrO_3-GBC (- - -). Scan rate 0.02 mV/s.

Two sets of the intercalation peaks on the XRD pattern for $ZnCl_2$-CrO_3-GBC (Fig. 1b), which arise from stage-6 $ZnCl_2$-GIC and stage-6 CrO_3-GIC, corroborates to this assumption.

The cyclic voltammogram (CV) obtained during the successive intercalation of H_2SO_4 into the $ZnCl_2$-GIC (the forward scan) followed by the deintercalation process (the reverse scan) is displayed in Fig. 4a. During the forward scan the anodic peaks related to the intercalation of HSO_4^-/H_2SO_4 into the graphite lattice are observed. The large irreversible anodic peak at about 1.02 V is recorded during the first forward scan after the completion of stage-1 $ZnCl_2$-H_2SO_4-GBC. No cathodic response to this peak is observed for the reverse scan, even down to - 0.6 V (not presented here). In such a situation it seems not justified to relate the anodic peak to the formation of graphite oxide. As reported previously, the giant anodic peak arising from the transformation of H_2SO_4-GIC to graphite oxide appears on CV curves in every cycle at a significantly higher potential of about 1.4 V and this peak is each time responded during the reverse scan[11]. The mentioned peak is observed neither during the anodic intercalation of HSO_4^- into the pure graphite[12,13] nor CrO_3-GIC[6,7,9], hence its origin might be related to the oxidation reaction in which the co-intercalated species, $ZnCl_2$ and H_2SO_4, take part. To explain this phenomenon thoroughly, further investigations are continued.

Some differences are noted during the successive intercalation/ deintercalation of HSO_4^- into the ternary $ZnCl_2$-CrO_3-GBC (Fig. 4b). A characteristic feature observed for the first forward scan are two cathodic leaps at 0.75 and 0.94 V. They are recorded after exceeding the anodic peak at 0.69 V (all the graphite galleries free of intercalate in the $ZnCl_2$-CrO_3-GBC are

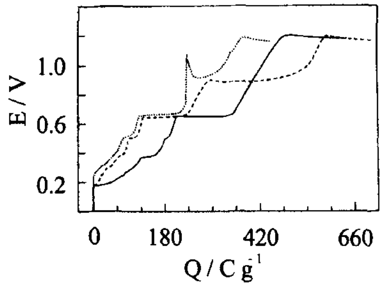

FIGURE 5 Galvanostatic oxidation in 18 M H_2SO_4 of graphite (——), $ZnCl_2$-GIC (- - -), $ZnCl_2$-CrO_3-GBC (······).

filled with H_2SO_4; stage-1 GIC). The explanation for these leaps is the invasion of H_2SO_4 into the graphite galleries occupied with CrO_3, resulting in the formation of the co-intercalation CrO_3-H_2SO_4 layer within $ZnCl_2$-CrO_3-H_2SO_4-GBC[6,7,9]. At about 1.02 V the anodic peak related to the interaction between the H_2SO_4 and $ZnCl_2$ intercalates appears. The decreased current of this peak, as compared to that in Fig. 4a, can be accounted for by smaller amount of $ZnCl_2$ in the $ZnCl_2$-CrO_3-GBC. On the galvanostatic curve (Fig. 5) the slopes and plateaux characteristic of the intercalation reactions of H_2SO_4 into the host lattice are observed. The potential plateau observed at about 0.9 V for $ZnCl_2$-GIC corresponds to the anodic peak on CV curve. For $ZnCl_2$-CrO_3-GBC the plateau is shifted to 0.92 V and the charge section is shortened in comparison with $ZnCl_2$-GIC. The decrease in charge can be ascribed to the deintercalated CrO_3 oxidiser the presence of which at the graphite/solution interface promotes the oxidation reaction. A sudden raise of the electrode potential, starting at about 0.7 V, well coincides with the cathodic leaps observed at CV curve during the first forward scan.

Acknowledgements

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