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Electrochemical Intercalation of $ZnCl_2$-CrO_3-GIC (Graphite Intercalation Compound) with Sulphuric Acid[*]

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The intercalation processes of CrO_3 and H_2SO_4 into $ZnCl_2$-GIC have been confirmed by X-ray diffraction analysis and voltammetric technique. The proposed mechanism of the intercalation of $ZnCl_2$-GIC with CrO_3 assumes the formation of co-intercalation domains within the interlayer spacings of the graphite structure. Upon the successive intercalation of the graphite compound with H_2SO_4, the peaks characteristic of $ZnCl_2$ and CrO_3 have been observed in the voltammogram. This is an evidence of the formation of quaternary $ZnCl_2$-CrO_3-H_2SO_4-GIC.

Key words: graphite intercalation compounds, bi-intercalation, electrochemical properties, zinc chloride, chromium(VI) oxide, sulphuric acid

One of the most disadvantageous properties of graphite intercalation compounds (GICs) is their relative instability and ease to decompose [1]. However, few of them are unusually stable, including CrO_3-GIC and CrO_2Cl_2-GIC. Croft was the first to obtain CrO_2Cl_2-GIC by allowing gaseous chromium(VI) oxychloride to react with graphite [2]. CrO_3-GIC is obtained using other methods, mainly by heating the mixture of graphite and molten chromium(VI) oxide [3–6], and by intercalation of graphite with chromium(VI) oxide, according to the procedure of Platzer and de la Martinierè [7]. This procedure is based on the reaction between graphite and chromium(VI) oxide mixed in glacial acetic acid. Recently, the mixture of chromium(VI) oxide and graphite in HCl was used to obtain GICs with Cr(VI) compounds: chromium(VI) oxide and chromium(VI) oxychloride, or other Cr(VI) compounds containing chlorine and oxygen [8]. The major advantage of this approach was the possibility to obtain GICs with the intercalate uniformly distributed between the graphite layers at the room temperature. This method was very simple and does not require any sophisticated equipment, yet the synthesis is time consuming.

Unoccupied spaces between the graphite layers in GIC (stage number $n \geq 2$) can be successively filled with another intercalate to obtain graphite bi-intercalation compound (GBC). CrO_3-GICs obtained by either Croft method or by Platzer and de la

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[*] Dedicated to Prof. Dr. Z. Galus on the occasion of his 70th birthday.

Martinierè method were extensively studied as the hosts for Brönsted acids: sulphuric [9–11] and perchloric [11,12]. GBCs intercalated with chromium(VI) oxide as the second compound were also obtained: $FeCl_3$-CrO_3-GBC [13], $ZnCl_2$-CrO_3-GBC [14]. Up to now, the intercalation of second guest into GIC applying the procedure described by Mittal *et al.* was not published.

In the present work, HCl solution was used to obtain CrO_3-GIC, which was further intercalated with sulphuric acid. $ZnCl_2$-CrO_3-GIC was also obtained by immersing $ZnCl_2$-GIC in the CrO_3/HCl solution. The product was next electrochemically intercalated with 95% sulphuric acid.

EXPERIMENTAL

In order to obtain the host stage-5 $ZnCl_2$-GIC (admixed with unreacted graphite), graphite flakes were intercalated with $ZnCl_2$ in 12 M aqueous solution of $ZnCl_2$ [14,15]. The intercalation process was carried out galvanostatically at 80°C applying current density of 4.0 mA/g. The obtained $ZnCl_2$-GIC was washed with acetone, dried and next immersed to the solution of CrO_3/HCl. Another sample was prepared by adding pure graphite (Graphitwerk Kropfmühl AG, Germany, average flake size: 180–200 μm) to the next CrO_3/HCl solution. The molar ratio of natural graphite and $ZnCl_2$-GIC to CrO_3 and 6 M HCl was 1:2 and 1:1, respectively. 6 M HCl solution was added to natural graphite or $ZnCl_2$-GIC in the molar ratios 1:1. This mixture of natural graphite (or $ZnCl_2$-GIC), CrO_3 and HCl was placed in the flask, closed and stored at the room temperature for 21 days. It was assumed that in the mixture comprising natural graphite and CrO_3/HCl solution CrO_3-GIC was formed. However, the studies on the chemical composition of the product were continued. The obtained products were washed with acetone and after that subjected to the voltammetric intercalation with 95% H_2SO_4 applying the scan rate of 0.1 mV/s and Hg/Hg_2SO_4/1 M H_2SO_4 reference electrode. Intercalation process was performed starting from the rest potential of the working electrode, up to the potential of 1.225 V. After that the potential was automatically decreased down to (–0.15 V) and de-intercalation process proceeded. XRD measurements were performed using the filtered CuKα radiation.

RESULTS AND DISCUSSION

It is known that the electrochemical oxidation of pure graphite in sulphuric acid leads to the formation of H_2SO_4-GIC [16–18]. In Figure 1a the forward scan in the cyclic voltammogram (CV) corresponds to the intercalation of graphite with HSO_4^-/H_2SO_4. The reverse scan corresponds to de-intercalation process. Anodic peaks in the CV should be assigned to the transformation process from the (n + 1) to n stage number (the stage number n is defined as the number of graphene layers between which intercalating molecules are accommodated). The main peak in the forward scan appears at 0.69 V and corresponds to the formation of stage-1 H_2SO_4-GIC. Further oxidation of stage-1 GIC is accompanied by the formation of the extended plateau, which corresponds to the ionization of sulphuric acid molecules accumulated within the interlayer spacings of graphite [16,17]. When the direction of the polarization is reversed, cathodic peaks are recorded, which refer to de-intercalation of the sulphuric acid.

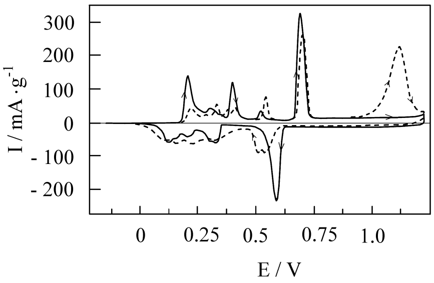

Figure 1. CV responses for intercalation/de-intercalation of 95% H_2SO_4 into/from (——) pure graphite, (a), (- - -) stage-5 $ZnCl_2$-GIC, (b).

Figure 1b presents the CV obtained during intercalation/de-intercalation of the host $ZnCl_2$-GIC with HSO_4^-/H_2SO_4. Anodic peaks in the forward scan correspond to intercalation of the graphite lattice with sulphuric acid. The most pronounced peak at 0.71 V refers to the formation of stage-1 $ZnCl_2$-H_2SO_4-GBC [14]. After the completion of this stage, a large irreversible anodic peak at *ca.* 1.12 V is observed. It is assigned to the oxidation of co-intercalating species, zinc chloride and sulphuric acid [14,19]. Noteworthy, this peak appears always in the first voltammetric scan during the subsequent intercalation with sulphuric acid, provided that zinc chloride intercalate is already incorporated into the graphite structure [20].

Another CVs recorded during intercalation/de-intercalation of HSO_4^-/H_2SO_4 into GIC are shown in Fig. 2. This time, however, before the measurement graphite was kept in the solution containing chromium(VI) oxide in 6 M hydrochloric acid. The first forward scan corresponding to the intercalation with sulphuric acid differs from the one recorded for pure graphite (Fig. 1a). In contrast to the situation presented in Fig 1a, after the completion of stage-1 GBC, a sudden drop in the anodic current is observed and two cathodic peaks at *ca.* 0.78 and 0.83 V are formed. It is reasonable to recall here, that similar phenomenon occurred during subsequent intercalation of CrO_3-GIC with HSO_4^-/H_2SO_4 performed by either the impregnation-dry method or the Platzer and de la Martiniere procedure. It has been already reported [9–11,21], that the appearance of cathodic signals in the anodic potential range is observed each time during the subsequent intercalation of CrO_3-GICs with HSO_4^-/H_2SO_4, if the forward scanning exceeds the potential of the formation of stage-1 GBC. At the beginning of the intercalation process, sulphuric acid molecules are being accommodated in the interlayer spacings of graphite free from chromium(VI) oxide until all of them are occupied. After that, HSO_4^-/H_2SO_4 are being co-intercalated in the interlayer spacings of graphite already filled with chromium(VI) oxide [9,21]. This results in the partial extrusion of chromium(VI) oxide from the peripheral regions of the graphite layers. The released chromium(VI) oxide undergoes reduction, which results in the above mentioned current jump to the cathodic range (Fig. 2). The latter can be thus regarded as the evidence of the presence of chromium(VI) oxide between the graphite layers in GIC. According to Mittal *et al.* [8], generation of GIC with chromium(VI) oxide from the mixture of graphite and chromium(VI) oxide in HCl solution is accompanied to some extent by the formation of chromium(VI) oxychloride or other Cr(VI) compounds containing oxygen and chlorine as the intercalates. After reversal of the polarization direction, several cathodic peaks referring to the removal of HSO_4^-/H_2SO_4 from the graphite lattice are observed. Similarly to H_2SO_4-GIC (Fig. 1a), the highest cathodic peak at 0.58 V (Fig. 2, first cycle) corresponds to the transformation of GIC from the stage-1 to the stage-2.

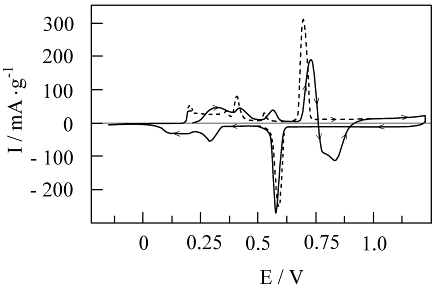

Figure 2. CV responses for intercalation/de-intercalation of 95% H_2SO_4 into/from GIC (obtained from the graphite/CrO_3/HCl mixture): cycle 1 (——), cycle 2 (- - -).

According to the XRD pattern presented in Fig 3a, the host $ZnCl_2$-GIC contains the stage-5 $ZnCl_2$-GIC ($I_c = 2.292$ nm) and the unreacted graphite (G 002 and G 004 peaks). The XRD pattern obtained after the intercalation of $ZnCl_2$-GIC with chromium(VI) oxide is shown in Fig. 3b. Comparing to Fig. 3a, the main difference is that no unreacted graphite is detected, whereas the stage number and the identity period ($I_c = 2.292$ nm) remain unchanged. The disappearance of the graphite phase after the insertion of the second intercalate into $ZnCl_2$-GIC may be attributed to the diffusion of chromium(VI) oxide through the interlayer spacings occupied by zinc chloride to the free spaces, where the formation of CrO_3-GIC occurs. The presence of the peaks characteristic for the stage-6 CrO_3-GIC ($I_c = 2.475$ nm, Fig. 3b) supports this hypothesis. Moreover, during the penetration of chromium(VI) oxide into the interlayer spacings filled with the primary intercalate (zinc chloride), co-intercalation may take place.

Figure 4 presents intercalation/deintercalation of GIC with HSO_4^-/H_2SO_4 obtained after the 21 day-lasting immersion of $ZnCl_2$-GIC to the solution of CrO_3/HCl. In the first forward scan, after the completion of the formation of stage-1 GBC, anodic current suddenly drops at *ca.* 0.77 V and cathodic signal appears. This indicates that the process of the subsequent intercalation of $ZnCl_2$-GIC with the secondary intercalate (chromium(VI) oxide) from the CrO_3/HCl solution has proceeded successfully. During further anodization of stage-1 GBC, a large irreversible anodic peak at *ca.* 1.13 V is recorded. This peak corresponds to the oxidation of co-intercalating species: zinc chloride and sulphuric acid. Its presence in the voltammogram confirms that after the subsequent intercalation of $ZnCl_2$-GIC with chromium(VI) oxide, the

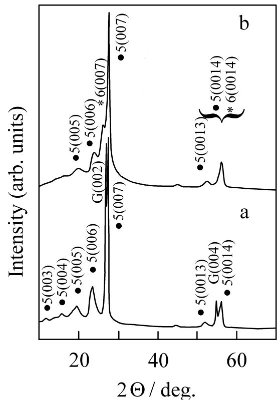

Figure 3. X-ray diffractogram of $ZnCl_2$-GIC (a), $ZnCl_2$-CrO_3-GIC (b) • stage-5 $ZnCl_2$-GIC, * stage-6 CrO_3-GIC, G – graphite.

primary intercalate (zinc chloride) is still present in the interlayer spacings of graphite. In the backward scan, the cathodic peaks related to de-intercalation of HSO_4^-/H_2SO_4 are observed. From the comparison of the backward scans in Fig. 1b and 4 it can be concluded that de-intercalation processes occur in a similar way for both $ZnCl_2$-H_2SO_4-GBC and $ZnCl_2$-CrO_3-H_2SO_4-GBC.

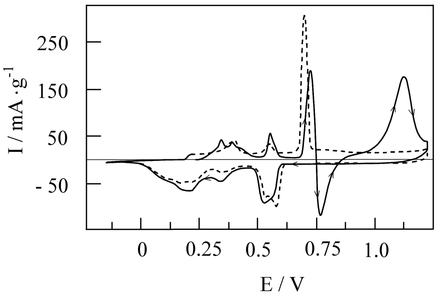

Figure 4. CV responses for intercalation/de-intercalation of 95% H_2SO_4 into/from $ZnCl_2$-CrO_3-GIC: cycle 1 (——), cycle 2 (- - -).

CONCLUSIONS

According to XRD results, one succeeded in the formation of $ZnCl_2$-CrO_3-GIC by the intercalation of chromium(VI) oxide into $ZnCl_2$-GIC from the mixture of $ZnCl_2$-GIC/CrO_3/HCl. The electrochemical behaviour of $ZnCl_2$-CrO_3-GIC, during the subsequent intercalation of HSO_4^-/H_2SO_4, confirmed the presence of both intercalates (zinc chloride and chromium(VI) oxide) in the graphite structure. One proposed the intercalation mechanism of $ZnCl_2$-GIC with chromium(VI) oxide, which assumes the formation of co-intercalating domains within the interlayer spacings of graphite. Moreover, during the intercalation of $ZnCl_2$-CrO_3-GIC with sulphuric acid, the formation of the quaternary $ZnCl_2$-CrO_3-H_2SO_4-GIC occurred. The original stage number of $ZnCl_2$-GIC was maintained for 21 days after the immersion of the compound to the CrO_3/HCl solution, which confirmed its high chemical stability.

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