

ELECTROCHEMICAL REACTIVITY OF THE CrO_3 -GRAPHITE SYSTEM IN AMMONIUM CHLORIDE SOLUTION

J. M. SKOWROŃSKI

*Technical University of Poznań, Institute of Chemistry and Applied Electrochemistry,
ul. Piotrowo 3, 60-965 Poznań (Poland)*

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Summary

The electrochemical reactivity of the CrO_3 -graphite intercalation compound (CrO_3 -GIC) is examined in 2 M NH_4Cl using a cyclic potentiodynamic method. The results have shown that the first discharge cycle differs from those ensuing. After the induction run the current peaks become more distinct and the reversibility of the redox reactions corresponding to chromium oxides increases upon cycling. The reasons for this behaviour are discussed in terms of the structural changes occurring within the intercalated graphite due to the electrochemical reactions. The results obtained are considered from the point of view of the application of CrO_3 -GICs in Leclanché-type cells and the prospects for rechargeability of the MnO_2 positive electrode.

Introduction

During recent years many systematic studies have been made on the electrochemical behaviour of graphite intercalated with chromium trioxide (CrO_3 -GIC) [1 - 9]. The papers published have reported the results obtained in aqueous acidic [2 - 7] as well as alkaline [8, 9] electrolytes. CrO_3 -GICs have appeared to be attractive materials for galvanic cells. The positive influence of CrO_3 -GICs on the electrochemical characteristics of MnO_2 cathodes has been observed both in acidic [6] and alkaline [8, 9] electrolytes. When pure graphite in the cathode mixture with manganese dioxide is replaced by its intercalation compound the electrical capacity of the cathode markedly increases. A very interesting feature has been noted in the studies on rechargeability of MnO_2 - CrO_3 cathodes in NH_4Cl solution [6]. The improvement of the first discharge capacity of the MnO_2 cathode due to the presence of CrO_3 -GICs in the cathode mixture has been observed only for some intercalation compounds of proper composition and structure whereas during the second discharge all CrO_3 -GICs have given rise to a significant increase in capacity.

The present paper yields new experimental data which enable us to understand this phenomenon.

Experimental

Materials and preparation

CrO₃-GIC designated A1-W1 was prepared by the impregnation-dry method discussed previously in detail [2, 3]. Reagent grade chromium trioxide produced by POCH Gliwice (Poland) and 99.7 wt.% C graphite flakes from Graphitwerke Kropfmühl AG (F.R.G.) were used without further purification. Sieve analysis data of the graphite used showed that about 95 wt.% flakes covered the size range 170 - 544 μm . The product of intercalation was purified with boiling water and hot 6 M HCl to remove unreacted CrO₃ and a physical phase of lower chromium oxides formed as a side-product [10]. Chemical analysis showed the C/Cr ratio of the purified product to be 28.1. A comprehensive discussion on the properties of the compound examined in this paper and on the methods used to evidence the intercalation has been presented in a recent paper [11].

Measurements

The construction of the experimental cell used in the present work was the same as that described earlier [1 - 5]. Electrochemical studies were performed in 2 M NH₄Cl whereas comparative measurements were performed in electrolytes containing a 1:1 mixture of 10⁻³ M Cr⁶⁺/Cr³⁺ or 10⁻³ M Cr³⁺ only, using K₂CrO₄ and CrCl₃ as reagents. The electrodes examined in this work were prepared in the form of a particle bed. The bed was placed in a cylindrical column on a Pt screen which served as the electrical contact and the bed support. At the top of the column a counter electrode of a Pt spiral was mounted. The potentials were measured against the saturated calomel electrode via a Luggin capillary filled with the electrolyte under investigation. All potentials in this paper are quoted *versus* NHE. The cyclic potentiodynamic measurements were performed with a scan rate of 1 mV s⁻¹. Unless otherwise stated, the runs were initiated at the rest potential of the working electrode and potential was changed in the anodic direction until a potential of 1200 mV was reached. Then the direction of polarization was reversed until a potential of -260 mV was attained. The weight of the electrodes was always 200 mg. All measurements were performed at 20 °C.

Results and discussion

Among the compounds discharged earlier in 2 M NH₄Cl [6] the sample designated A1-W1 has the maximum concentration of chromium. Based upon many properties characteristic of GICs this sample has been recognized as an intercalation compound of disordered structure [3, 11, 12]. In the

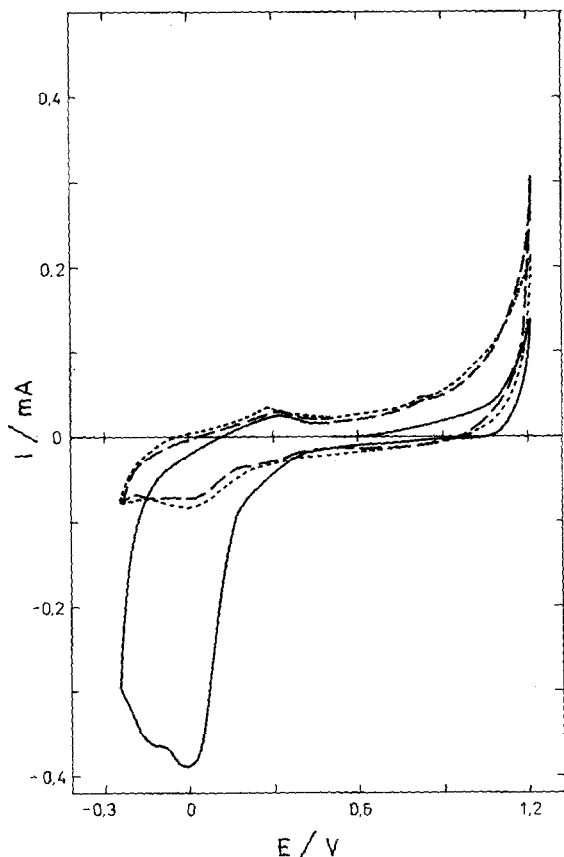


Fig. 1. Cyclic potentiodynamic curves of pristine graphite (sample A1) obtained in 2 M NH_4Cl : —, cycle 1; ---, cycle 2, - · - ·, cycle 3.

previous paper [6] it was demonstrated that this compound distinctly improves the capacity of the MnO_2 -graphite- CrO_3 -GIC cathode only after the first activating charge. The mentioned properties encouraged us to subject this compound to potentiodynamic measurements.

During the first reverse sweep the pristine graphite used for intercalation with CrO_3 demonstrates a double cathodic peak (at 10 and -140 mV) whereas on the anodic curve a small peak at about 324 mV is noted (Fig. 1). The cathodic peak diminishes abruptly during the second sweep and remains almost unchanged during the following cycles. In addition, the current of the anodic peak changes insignificantly with cycling. In the light of the earlier results [2, 13] the presence of peaks which do not change with cycling can be attributed to the redox reactions of the oxygen complexes of graphite. However, the double cathodic peak of the first cycle seems to have a different origin, because a large cathodic peak of the same shape and intensity also appears when the runs are started from the rest potential of the electrode directly towards the negative potentials. Thus one can infer

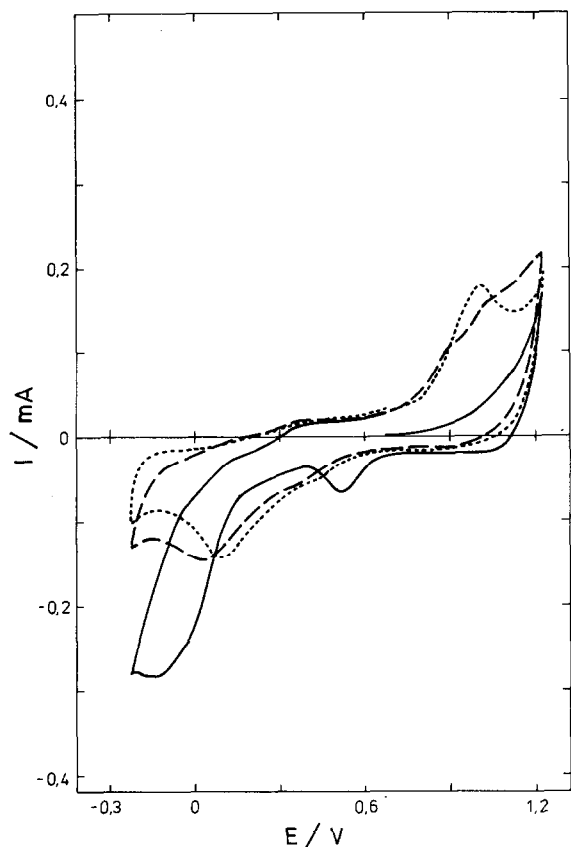


Fig. 2. Cyclic potentiodynamic curves of graphite intercalation compound (sample A1-W1) obtained in 2 M NH_4Cl : —, cycle 1; - - -, cycle 2; · · ·, cycle 3.

that the peak does not result from the reduction of the product of the electrochemical oxidation of graphite but is rather related to the reduction of oxygen adsorbed at the graphite edges and fissures. A separate experiment showed that if the sweep range is shortened and the measurements are restricted to a narrow potential range (from the rest potential to -260 mV) then the large peak of the first cathodic will be a single one. However, during the following cycles, the intensity of the peaks attributed to the reactions of the carbon-oxygen complexes became smaller in intensity by about 50% as compared with those formed when the potential of reversion of 1200 mV is used. This result suggests that the double cathodic peak observed in the first complete cycle carried out between 1200 and -260 mV follows from the superposition of two reactions: the reduction of the adsorbed oxygen as well as the reduction of the carbon-oxygen complexes, respectively.

The potentiodynamic curves noted for the intercalation compound (Fig. 2) differ distinctly from those in pristine graphite. During the first sweep, apart from the large cathodic peak characteristic of pristine graphite,

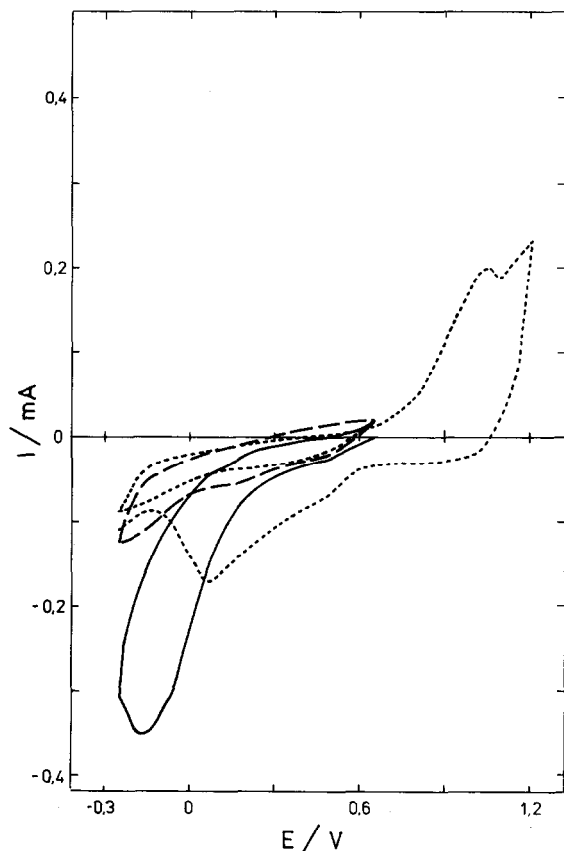


Fig. 3. Cyclic potentiodynamic curves of graphite intercalation compound (sample A1-W1) obtained in 2 M NH_4Cl : —, cycle 1; ---, cycle 2; - · - · -, cycle 3; · · · ·, cycle 4. Note three cycles scanned from the rest potential to -260 mV.

a new cathodic peak at 490 mV is noted and upon cycling the following peaks appear. In the second cycle a distinct cathodic peak at 6 mV is noted and, in turn, on reversing the direction of polarization, a broad anodic peak is formed at about 980 mV. This peak is markedly shaped during the next scan. On the other hand, one can see in Fig. 2 that upon cycling the position of the cathodic peak shifts towards more positive potentials. The fact that the anodic peak in curves in Fig. 2 becomes more and more well shaped on cycling could answer the question why the discharge capacity of the MnO_2 - CrO_3 -GIC cathode increases during the second discharge as compared with the value obtained for the first discharge [6]. To explain the reactions occurring within the current peaks we have performed the following test. First, the compound was scanned from the rest potential of the electrode in the cathodic direction down to -260 mV and after three shortened cycles the complete cycle was carried out (Fig. 3). As one can see from the Figure the cathodic pretreatment leads to the formation of a well shaped anodic

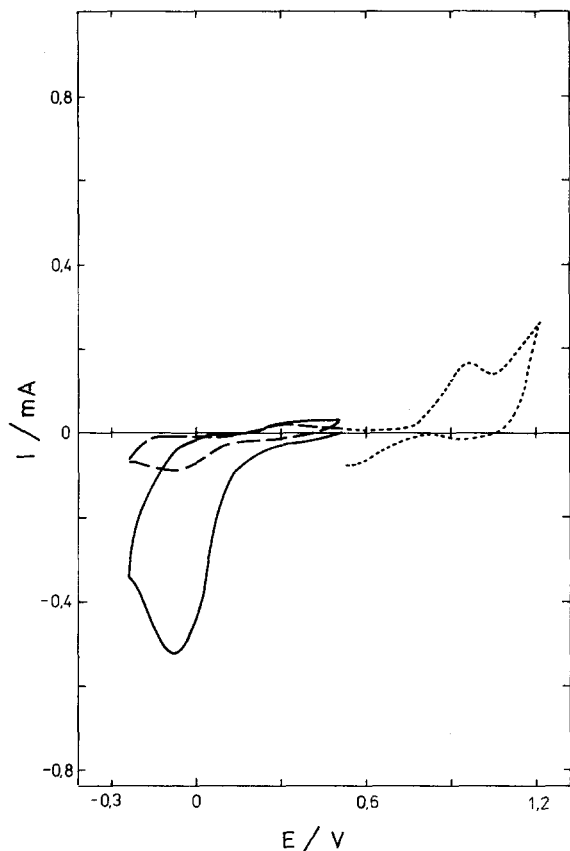


Fig. 4. Cyclic potentiodynamic curves of pristine graphite (sample A1) obtained in 2 M NH_4Cl containing 10^{-3} M Cr^{3+} as CrCl_3 : —, cycle 1; ---, cycle 2; ···, cycle 3. Note two cycles scanned from the rest potential to -260 mV.

peak at about 1.0 V already during the first scan carried out up to 1.2 V. During the reverse potential sweep a cathodic peak at 58 mV is recorded. The result of this test confirms that the anodic peak in the potentiodynamic curves is the response from the cathodic reactions of CrO_3 -GIC. The contribution to the mechanism of reaction for pure graphite in the standard electrolyte admixed with 10^{-3} M Cr^{3+} gives the results shown in Fig. 4. On scanning the sample in the potential range from the rest potential to -260 mV (two cycles) no new peaks, except these obtained for pristine graphite in the electrolyte free of chromium ions, were recorded. This shows that in the scanned range of potentials no further reduction of Cr^{3+} takes place. During the third cycle, from the rest potential to 1200 mV, a distinct peak at 980 mV is noted which can be attributed to the oxidation of Cr^{3+} to Cr^{6+} [14].

Further measurements which could account for the mechanism of the reactions occurring within CrO_3 -GICs were carried out using pure graphite

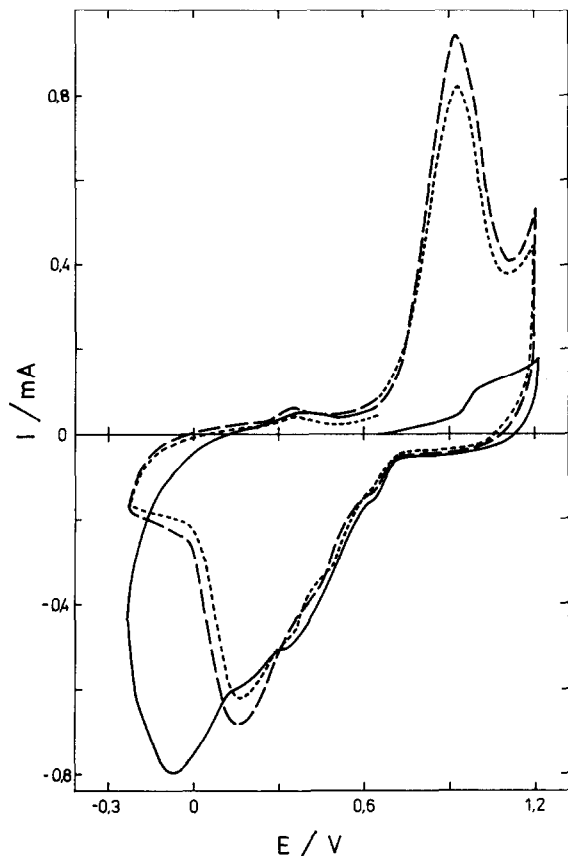


Fig. 5. Cyclic potentiodynamic curves of pristine graphite (sample A1) obtained in 2 M NH_4Cl containing 1:1 mixture of 10^{-3} M Cr^{6+} and Cr^{3+} : —, cycle 1; ---, cycle 2; ···, cycle 3.

in the standard electrolyte containing 10^{-3} M $\text{Cr}^{6+}/\text{Cr}^{3+}$ (1:1). In the curves presented in Fig. 5 the anodic and cathodic peaks associated with the redox reactions of the chromium ions present in the electrolyte are visible and they are, to some extent, similar to those recorded for CrO_3 -GIC in pure electrolyte (Fig. 2). Such a similarity could suggest that the peaks obtained for the intercalation compound result from chromium ions which appeared in the electrolyte already before the runs were initiated as the effect of chemical dissolution of the compound. If so, the increase in the peaks intensity should be noted in the case when the intercalation compound placed in the electrochemical cell is immersed in the electrolyte for a longer time before the measurements. However, this explanation must be rejected because the same peak positions and the same peaks currents have been obtained for very different periods of immersion, *e.g.*, 0.5 and 24 h.

Comparison of Figs. 2 and 5 shows that it is unlikely that the anodic peak recorded for CrO_3 -GIC at about 1.0 V arises from the oxidation of

chromium ions of the valency lower than six dissolved from the compound before the measurements are started. As can be seen, for pristine graphite examined in electrolyte containing chromium ions purposely added the anodic peak is recorded already during the first run (Fig. 5) whereas for CrO_3 -GIC scanned in pure electrolyte this peak does not appear before the third cycle (Fig. 2). For both cases there are also considerable differences in the peak positions. Considering, for example, the third cycles, one can see that for pristine graphite in the electrolyte containing the $\text{Cr}^{6+}/\text{Cr}^{3+}$ couple the anodic peak appears in more negative potential (901 mV) whereas the cathodic peak is recorded in more positive potential (116 mV) as compared with the peaks observed for CrO_3 -GIC in pure electrolyte (980 and 40 mV, respectively). This means that the redox reactions of the chromium ions dissolved in the electrolyte are more reversible than those preceding with the intercalation compound. Finally, chemical analysis confirmed that the intercalation compound was resistant to the electrolyte. In the earlier papers [2 - 5] it was reported that the compound examined in the present work is not affected by solutions of HCl and H_2SO_4 . The differences referring to the mechanism of reactions occurring in both cases discussed above are also reflected in the curves obtained for the intercalation compound examined in 2 M $\text{NH}_4\text{Cl} + 10^{-3}$ M $\text{Cr}^{6+}/\text{Cr}^{3+}$ (Fig. 6). The presence of chromium ions in the electrolyte resulted in broadening of the peaks, especially the cathodic ones, which is effected by the superposition of the peaks associated with the reactions of the chromium ions present in the electrolyte and the reactions of the intercalation compound. The absence of the anodic peak for the first scan in Fig. 6 is probably caused by chemical oxidation of Cr^{3+} by CrO_3 -GIC occurring at the electrolyte-solid electrode interface.

Upon cycling the differences in the potentiodynamic curves obtained for pristine graphite in the electrolyte containing chromium ions and for the intercalation compound in the pure electrolyte become more and more noticeable. By comparison, in the latter case the cathodic peak is shifted towards more positive potentials. Figure 7 illustrates the changes in the potentiodynamic curves referring to the third cycles.

The results presented above allow us to propose the following mechanism of the reactions of CrO_3 -GIC in 2 M NH_4Cl . The first point worth noting is that the formation of the hexavalent chromium corresponding to the anodic peak at about 1 V must be preceded by reduction of the compound down to -0.26 V. For understanding the mechanism of reactions occurring within the intercalation compound the fact that the cathodic peak shifts towards more positive potentials upon cycling can have a great importance. To approach this problem, it is appropriate at this point to recall some properties of the examined compound. The results published in previous papers have shown [3, 5, 11, 12] that the compound is of a disordered structure in which the intercalant is distributed non-uniformly and probably enclosed within the graphite pockets. This property can make the access of electrolyte to the more inner regions of graphite more difficult. Based on thermodynamic data [14] it is likely that during the reduction

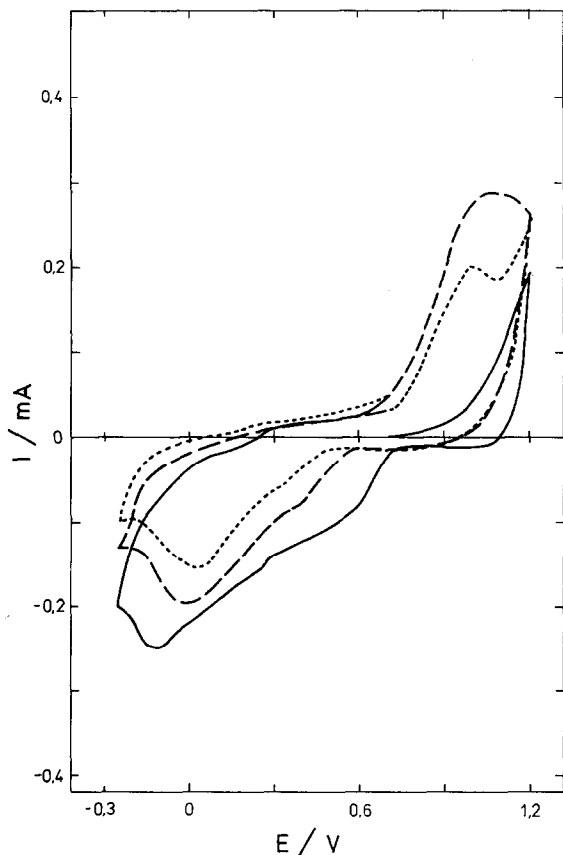


Fig. 6. Cyclic potentiodynamic curves of graphite intercalation compound (sample A1-W1) obtained in 2 M NH_4Cl containing 1:1 mixture of 10^{-3} M Cr^{6+} and Cr^{3+} : —, cycle 1; ---, cycle 2; ···, cycle 3.

reactions occurring in 2 M NH_4Cl the intercalant is converted to $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$. Because the OH^- and Cr^{3+} ions formed on reduction are greater in diameter than the former O^{2-} and Cr^{6+} ions the graphite interspaces containing the intercalant could expand. This may result in exfoliation of the compound which increases the reactive surface of the electrode. Consequently, the activity of the electrode increases. Similar changes in the structure of CrO_3 -GIC have been suggested earlier as being responsible for anomalous changes appearing in the galvanostatic curves obtained during reduction in alkaline electrolyte [8, 15]. The process of electrochemical exfoliation can also account for the changes observed in the potentiodynamic curves. Exfoliation, through the disruption of the graphite pockets, facilitates the diffusion of electrolyte into the more inner graphite regions and allows the molecules of the intercalant previously blocked to take part in the reaction. This interpretation could answer the question why the discharge capacity of the MnO_2 - CrO_3 -GIC cathode obtained during galvanostatic measurements

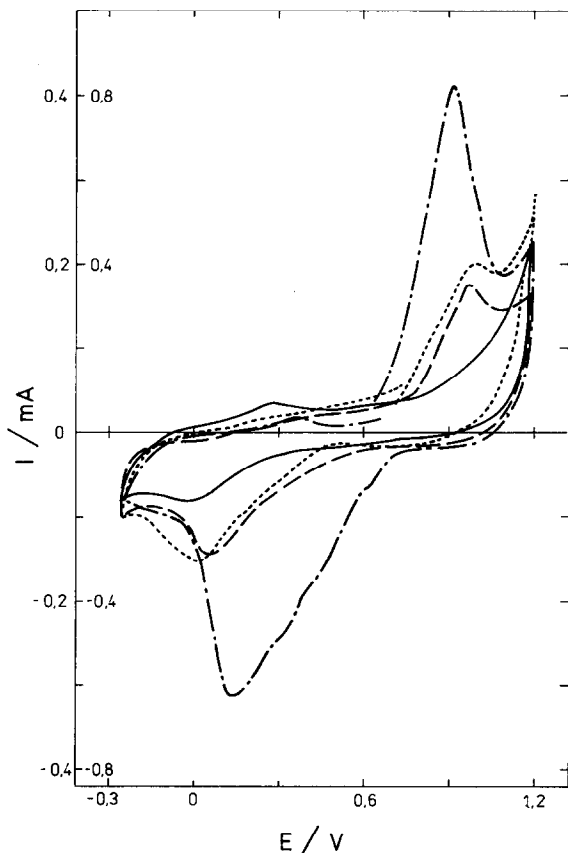


Fig. 7. Comparison of the third cycles of pristine graphite and graphite intercalation compound obtained in 2 M NH_4Cl without and with 1:1 mixture of 10^{-3} Cr^{6+} and Cr^{3+} : —, pristine graphite in pure electrolyte; ---, graphite intercalation compound in pure electrolyte; - · - · -, pristine graphite in electrolyte containing chromium ions; · · · · -, graphite intercalation compound in electrolyte containing chromium ions.

[6] is higher for the second discharge as compared with that of the first discharge. The increase in the electrochemical activity of the compound on cycling could also be the reason for the shift in the potential of the reduction peak. According to the literature [14], it is probable that a slight part of the product of reduction, $\text{Cr}(\text{OH})_3 \cdot n\text{H}_2\text{O}$, is dissolved by the electrolyte and, hence, the soluble CrOH^{2+} can leave the graphite interspaces. Consequently, the released ions of the trivalent chromium are, upon the anodic sweep, oxidized to the chromate ions giving the characteristic peak at about 1 V. On the other hand, it cannot be excluded that the other part of the reduced intercalant is undissolved and remains within the graphite structure to, in turn, take part in the oxidation reactions to chromates. The presence of the intercalated chromates in CrO_3 -GICs has been suggested previously [16]. In the next paper [17] the structural aspect of the changes occurring in CrO_3 -

GIC during the discharge-charge cycles is considered using a compound with a higher concentration of chromium ($C/Cr = 13.6$) and of a more ordered structure [11].

Acknowledgement

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