

# Influence of heat treatment of CrO<sub>3</sub>-graphite intercalation compounds on subsequent electrochemical intercalation of sulphuric acid

J. M. SKOWROŃSKI

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

Received 6 November 1992; revised 5 July 1993

A sudden cathodic jump appearing on the potentiodynamic curves during subsequent electrochemical intercalation of 18 M sulphuric acid into chromium trioxide-graphite intercalation compounds (CrO<sub>3</sub>-GICs) is preserved for CrO<sub>3</sub>-GICs heated at a temperature lower than that of the decomposition of the intercalate, but vanishes completely after CrO<sub>3</sub>-GICs are thermally transformed into the physical mixture of graphite and lower chromium oxides. The results have shown that CrO<sub>3</sub>-GICs can be prepared, not only by the solvent method but also by the impregnation-dry method. Using a potentiodynamic technique involving the thermal modification of CrO<sub>3</sub>-GICs it has been possible to demonstrate the presence of an intercalation phase for CrO<sub>3</sub>-GICs which have unclear X-ray diffraction patterns.

## 1. Introduction

It is well known that the intercalation of sulphuric acid into graphite can occur by chemical as well as electrochemical methods. To prepare the intercalation compound (H<sub>2</sub>SO<sub>4</sub>-GIC) using the former method the presence of oxidizers, for example CrO<sub>3</sub>, HNO<sub>3</sub>, KMnO<sub>4</sub>, is necessary in the solution [1, 2].

The influence of the oxidizers on the intercalation reaction has been quantitatively explained by Inagaki *et al.* [3, 4]. These authors concluded that the chemical process is fundamentally the same as the electrochemical one and that the oxidizers dissolved in the solution oxidize the pristine graphite, fixing the threshold potential at which the following stage of H<sub>2</sub>SO<sub>4</sub>-graphite compound is subsequently formed. Using the electrochemical method, the preparation of stage 1 H<sub>2</sub>SO<sub>4</sub>-GIC can also be accelerated by adding chromium trioxide to sulphuric acid [5]. Very surprising phenomena have been observed in 18 M sulphuric acid when the starting material is the intercalation compound with chromium trioxide (CrO<sub>3</sub>-GIC) instead of pure graphite [5, 6]. Apart from the peaks associated with the stage transformation of H<sub>2</sub>SO<sub>4</sub>-GIC, on the potentiodynamic curve a dramatic cathodic jump has been recorded during the first positive scan when the potential corresponding to the formation of stage 1 H<sub>2</sub>SO<sub>4</sub>-graphite compound is reached. *In situ* electrical conductivity measurements have shown that the cathodic jump is accompanied by a sudden conductivity drop [6]. These effects have been assumed to arise from the reaction of sulphuric acid with the CrO<sub>3</sub> intercalated in graphite. The present work gives new experimental data which support this explanation and makes the

mechanism of cointercalation more clear. It is shown that using the potentiodynamic method the intercalation phase can be identified in the disordered and diluted CrO<sub>3</sub>-GICs formed thermally from the well-ordered ones, despite the almost total disappearance of the intercalation lines in the X-ray diffraction pattern.

## 2. Experimental details

CrO<sub>3</sub>-GICs were prepared by both the solvent (sample A2-AC) and impregnation-dry (sample A1-W1) methods. Intercalation by the former method was carried out according to the procedure of Platzler and de la Martinière [7], using a mixture of 1 g graphite and 5 g CrO<sub>3</sub> in 50 cm<sup>3</sup> glacial acetic acid. The product was washed with acetone and dried to constant weight. The procedure of the impregnation-dry method has been described earlier [8, 9]. The preparation and the chemical data of both CrO<sub>3</sub>-GICs have been reported previously [5].

To determine the electrochemical changes effected by heat-treatment the samples of CrO<sub>3</sub>-GICs were heated to 160 and 240°C, respectively. The thermal characteristics of the samples are presented in Fig. 1 and in Table 1.

X-ray diffraction analysis of the original and the heat-treated compounds was performed using CuK<sub>α</sub> radiation (Fig. 2).

The electrochemical studies were performed in 18 M H<sub>2</sub>SO<sub>4</sub> using a working electrode in the form of particle bed placed on a platinum screen. To ensure a good electrical contact between the graphite particles, a short glass cylinder, closed at the bottom by polypropylene fibre, was placed at the top of the

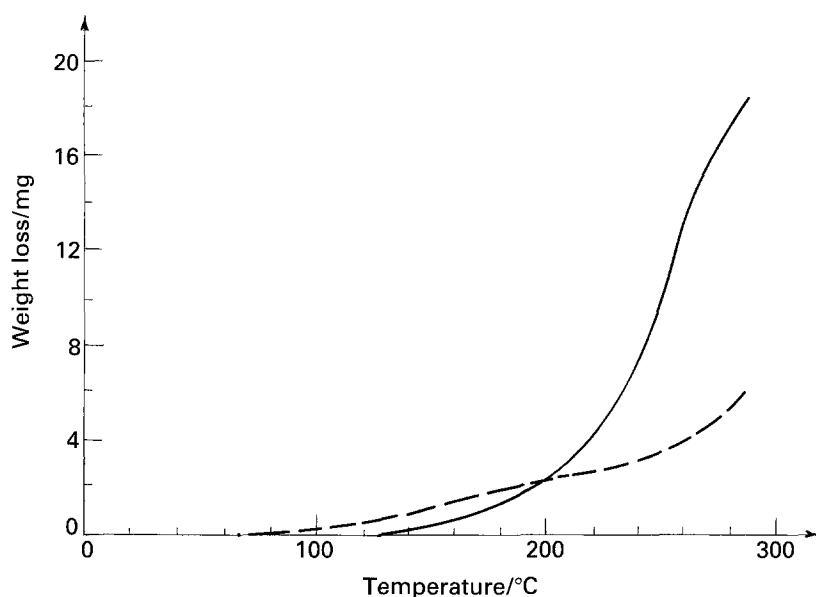


Fig. 1. Thermogravimetric curves of  $\text{CrO}_3$ -GICs recorded in argon. Sample weight: 800 mg, heating rate:  $10^\circ \text{ min}^{-1}$ . (—)  $\text{CrO}_3$ -GIC prepared by the impregnation-dry method (sample A1-W1); (---)  $\text{CrO}_3$ -GIC prepared by the solvent method (sample A2-AC).

electrode. The counter electrode was a platinum spiral, whereas the reference electrode was  $\text{Hg}/\text{Hg}_2\text{SO}_4$  with 1 M  $\text{H}_2\text{SO}_4$  connected to the solution under investigation by a Luggin capillary. Potentials measured against this electrode are designated  $E$  in Figs 3–5 of this paper. Cyclic potentiodynamic runs with a scan rate of  $0.1 \text{ mV s}^{-1}$  were initiated at the rest potential of the electrode and the potential was changed in the positive direction up to 1.15 V. Then the direction of polarization was reversed and the potential was lowered to  $-0.2 \text{ V}$ . All measurements were performed at a temperature of  $20^\circ \text{ C}$  using an electrode weight of 50 mg.

### 3. Results and discussion

The replacement of the pristine graphite by  $\text{CrO}_3$ -GIC leads to the appearance of striking effects on the potentiodynamic curves (Fig. 3). During the first forward sweep, when the potential of the stage 1  $\text{H}_2\text{SO}_4$ -GIC is nearly reached (around 0.9 V), the current falls abruptly towards the cathodic region to return to the anodic current side. After the reversal of polarization a multiple cathodic response (with two maxima at 0.65 and 0.8 V, respectively, and an inflexion point at about 1 V) appears for both  $\text{CrO}_3$ -GICs within the potential region where the plateau is recorded for the pristine graphite. The origin of the cathodic current jump has been

accounted for by the opening of the graphite 'pockets' (encapsulating the intercalated  $\text{CrO}_3$  followed by the reaction of the primary intercalate with  $\text{H}_2\text{SO}_4$  [5, 6]. A multiple cathodic peak response during the reverse sweep in the range between 0.5 and 1.15 V has been assumed to arise from the reduction of  $\text{CrO}_3$  released from and/or retained within the graphite lattice [5]. If we take into account the results reported earlier [10, 11] that sample A2-AC (prepared by the solvent method), exhibiting X-ray diffraction pattern with a family of intercalation peaks, is more easily deintercalated in aqueous electrolytes than sample A1-W1 (prepared by the impregnation-dry method) having a very disordered structure, then greater amounts of structural traps existing in the latter sample may be responsible for the fact that the mentioned cathodic response of sample A1-W1 does not disappear after the first reverse sweep, as in the case of sample A2-AC (Fig. 3), but is preserved for three cycles. In addition, a distinct depression is observed for the second and third cycles of sample A1-W1 at potentials higher than 1 V which may correspond to the second step of cointercalation of  $\text{H}_2\text{SO}_4$  into the host  $\text{CrO}_3$ -GIC. More recently it has been shown that during the first forward sweep in 12 M  $\text{H}_2\text{SO}_4$  three cathodic jumps are recorded for sample A1-W1 but only one jump for sample A2-AC [12]. Such different behaviour of both samples is attributed to the chemical and structural properties of  $\text{CrO}_3$ -GICs resulting from the method of intercalation.

A distinct weight loss of  $\text{CrO}_3$ -GICs observed on the thermogravimetric curves above  $220^\circ \text{ C}$  (Fig. 1) is associated with the deintercalation of  $\text{CrO}_3$ -GIC resulting from the thermal decomposition of  $\text{CrO}_3$  alone to lower chromium oxides [13, 14] and from its reduction by graphite carbons [9, 15–17]. Above  $220^\circ \text{ C}$   $\text{CrO}_3$ -GICs change into exfoliated graphite [9, 11, 15, 17, 18] formed due to the rupture of the graphite cages retaining the intercalated islands. It has been shown previously that the intercalation

Table 1. Weight loss of  $\text{CrO}_3$ -GICs obtained by the thermogravimetric method

Sample ( $\text{IC} = \text{Cr}/\text{C}$ ) $\times 10^3$	Weight loss				
	at $160^\circ \text{ C}$		at $240^\circ \text{ C}$		
	$\Delta m$ /%	$\Delta m/\text{IC}$ /%	$\Delta m$ /%	$\Delta m/\text{IC}$ /%	
A2-AC	22.8	0.17	7.46	0.39	17.1
A1-W1	35.6	0.07	1.97	0.91	25.6

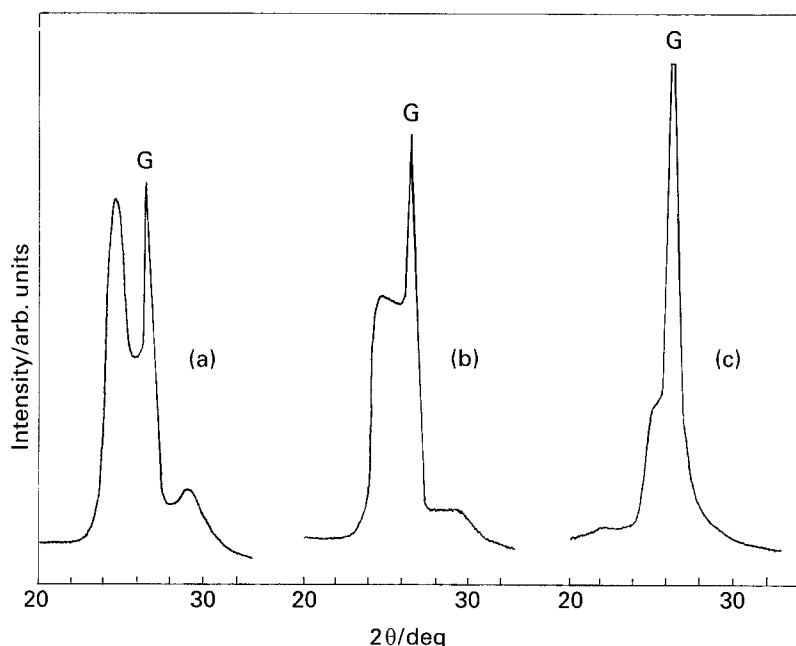


Fig. 2. X-ray diffraction patterns of CrO<sub>3</sub>-GIC prepared by the solvent method (sample A2-AC). G = graphite 002 reflection. (a) original compound; (b) after heat treatment at 160°C for 10 min; (c) after heat treatment at 160°C for 1 h. Nickel filtered CuK<sub>α</sub> radiation.

peaks on X-ray diffractograms disappear instantly on heating CrO<sub>3</sub>-GICs above 220°C [11]. The TG curves presented in Fig. 1 also show that the weight loss of both compounds begins at temperatures distinctly lower than 200°C. Below 200°C sample A2-AC is markedly less stable than sample A1-W1. Taking into account the results of Kobayashi *et al.* [19] it may be assumed that, in the case of CrO<sub>3</sub>-GIC

from the solvent method (A2-AC), CO<sub>2</sub> may also originate from the decomposition of the CH<sub>3</sub>COOH molecules cointercalated with CrO<sub>3</sub>. It is interesting to note that the weight loss,  $\Delta m$ , is not simply proportional to the amount of the intercalated CrO<sub>3</sub>, but also depends on the structure of CrO<sub>3</sub>-GIC resulting from the method of intercalation (parameter  $\Delta m/IC$  in Table 1).

In Fig. 2 the structural changes caused by heating a CrO<sub>3</sub>-GIC (sample A2-AC) below the decomposition temperature are shown. Intercalation peaks decrease in intensity and become broader with the time of heat-treatment. After 1 h only one residual intercalation peak is visible (Fig. 2(c)). This diffractogram resembles that of the original CrO<sub>3</sub>-GIC prepared by the impregnation-dry method exhibiting only one broad and small nongraphite peak (sample A1-W1) [9, 20].

The most characteristic feature of the potentiodynamic curves obtained for both CrO<sub>3</sub>-GICs decomposed at 240°C is the disappearance of the cathodic jump. This result shows that this effect is associated with the reactions occurring within the intercalated phase of graphite. As can be seen from Fig. 4, a double anodic peak appears in the potential range 0.65–0.95 V instead of the cathodic leap. On cycling the two peaks become more pronounced. The comparison of this figure with those recorded for the pristine graphite [5, 6, 21–23] leads to the following conclusion. As the first current subpeak appearing in Fig. 4 at less positive potential (the maximum at about 0.8 V) is associated with the transformation from stage 2 to stage 1 H<sub>2</sub>SO<sub>4</sub>-GIC, the second one can be assumed to arise from the anodic oxidation of lower chromium oxides produced due to the thermal decomposition of CrO<sub>3</sub>-GIC. The current rise observed above 1 V is associated with the overoxidation reaction of graphite. After the polarization is reversed, a large double cathodic peak is recorded in the potential range around

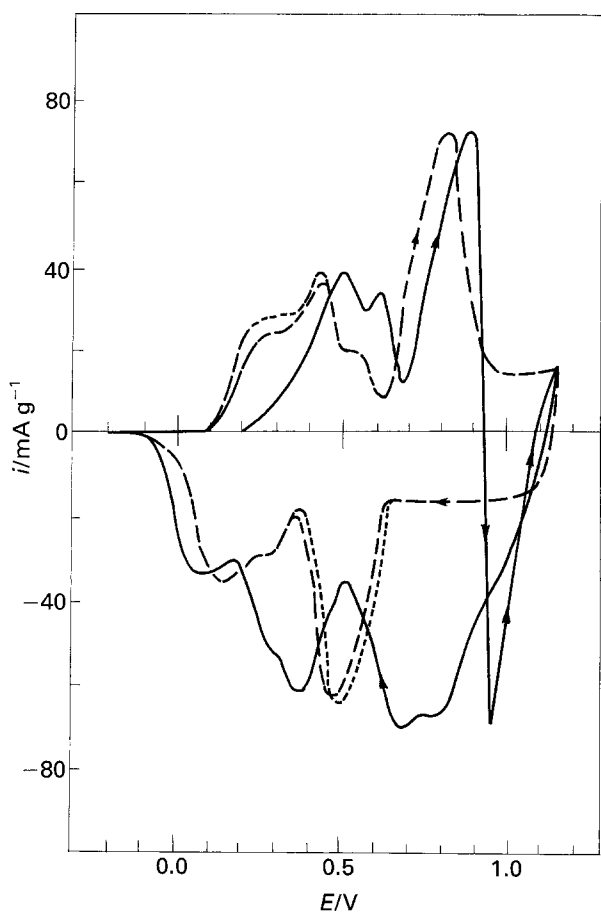


Fig. 3. Cyclic potentiodynamic curves obtained in 18 M H<sub>2</sub>SO<sub>4</sub> for CrO<sub>3</sub>-GIC (sample A2-AC). (—) Cycle 1; (---) cycle 2; (- - -) cycle 3.

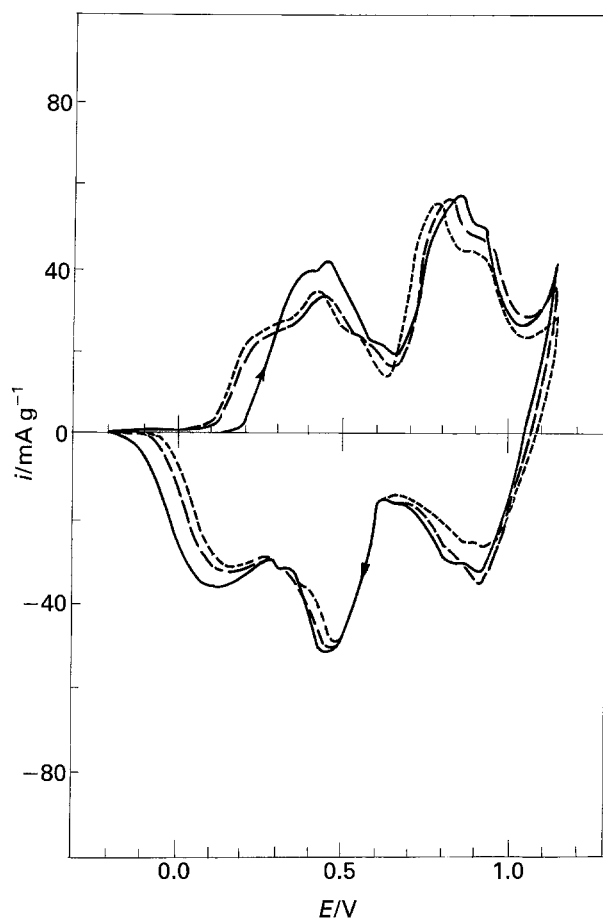


Fig. 4. Cyclic potentiodynamic curves obtained in 18 M  $\text{H}_2\text{SO}_4$  for  $\text{CrO}_3$ -GIC (sample A2-AC) heated at  $240^\circ\text{C}$  for 3 h. (—) Cycle 1; (---) cycle 2; (- - -) cycle 3.

0.6–1 V. This peak is similar to that observed for the original  $\text{CrO}_3$ -GICs (Fig. 3) except for the fact that in the case of the products of thermal decomposition of  $\text{CrO}_3$ -GICs no inflexion is recorded on its right branch. Two reactions proceeding within this peak may be related to the reduction of the overoxidized graphite, as well as the reduction of  $\text{Cr}^{6+}$ .

To understand more thoroughly the participation of lower chromium oxides in the electrochemical reactions in 18 M  $\text{H}_2\text{SO}_4$  it is important to recall that two types of oxides, incorporated with the graphite lattice and being a physical admixture, have been distinguished [24, 25]. The latter oxides are formed at temperatures higher than the equilibrium temperature of  $\text{CrO}_3/\text{Cr}_3\text{O}_8$  (over  $220^\circ\text{C}$ ) [13] when the intercalated  $\text{CrO}_3$  decomposes and is reduced by the graphitic carbons. Due to these reactions the intercalation compound is completely destroyed with the accompanying exfoliation effect. At temperatures lower than  $200^\circ\text{C}$  the intercalated  $\text{CrO}_3$  is reduced exclusively by the graphitic carbons [17], preferably at the edges of graphite flakes and at the structural defects. In consequence, new graphite pockets are formed in which the  $\text{CrO}_3$  intercalate is surrounded by reduced molecules of oxidation state between 3.8 and 5.2 [25].

Figure 5 shows the changes in the potentiodynamic curves resulting from heat-treatment of  $\text{CrO}_3$ -GIC (sample A2-AC) at  $160^\circ\text{C}$ . A sharp current jump at

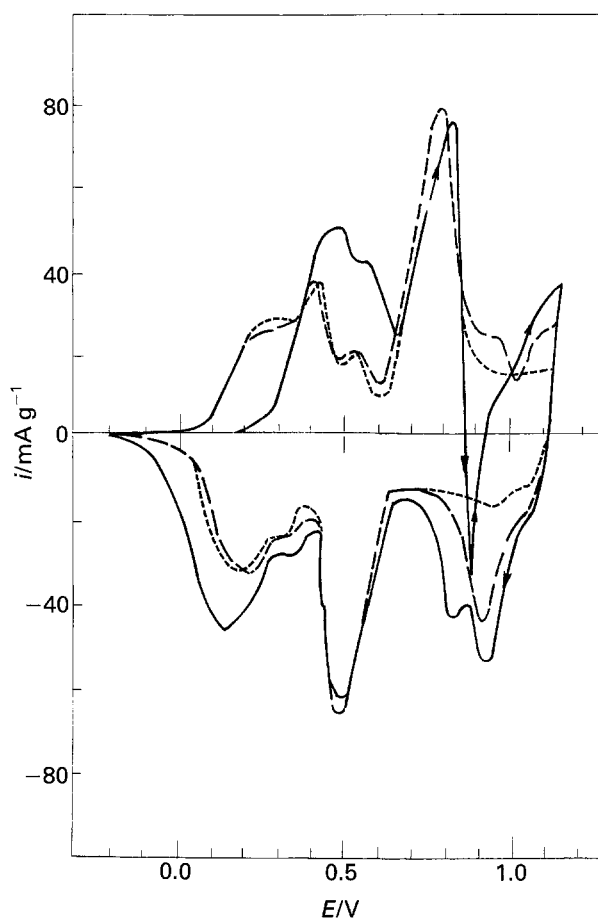


Fig. 5. Cyclic potentiodynamic curves obtained in 18 M  $\text{H}_2\text{SO}_4$  for  $\text{CrO}_3$ -GIC (sample A2-AC) heated at  $160^\circ\text{C}$  for 1 h. (—) Cycle 1; (---) cycle 2; (- - -) cycle 3.

about 0.85 V is still observed but its amplitude is reduced as compared with that recorded for the original  $\text{CrO}_3$ -GICs (Fig. 3). This suggests the loss of some intercalated molecules of  $\text{CrO}_3$  due to their reduction by the graphitic carbons. The remaining intercalate remains with the same structure and/or can form new intercalation domains of mixed stages containing chromium of lower oxidation state. Thus, consistent with the previous findings [10, 11, 17, 18, 24] and supported by Fig. 2, a new diluted and disordered intercalation system, admixed with non-bonded lower chromium oxides, is formed on heating  $\text{CrO}_3$ -GICs at  $160^\circ\text{C}$ . Despite the almost total disappearance of the intercalation peaks upon prolonged heating of sample A2-AC from 10 min to 1 h (Fig. 2(c)), the sharp cathodic jump is still present on the potentiodynamic curve of this sample (Fig. 5), but it is of lower intensity. The cathodic jump was also observed on the potentiodynamic curve obtained for sample A1-W1 heated *prior* to the measurements for 1 h. The thermoelectrochemical characterization of  $\text{CrO}_3$ -GICs provides new evidence that graphite can be intercalated with  $\text{CrO}_3$  by the impregnation-dry method and shows that the potentiodynamic method involving the cathodic current effect is a very sensitive tool allowing the detection of chromium oxides intercalated in the disordered and diluted systems for which X-ray analysis fails. These results, at variance with the

claims of Ebert *et al.* [14, 26, 27], support the previous statement [5, 11, 24] that the absence in the X-ray pattern of the intercalation lines is not proof that the product of intercalation contains no intercalation phase.

The characteristic feature of the potentiodynamic curves obtained for all CrO<sub>3</sub>-GICs heated at 160°C is the depression recorded at about 1 V during the forward sweep (Fig. 5). As mentioned above, a similar depression, but of smaller amplitude, was noted for the pristine compound marked A1-W1. However, after this sample was heated at 160°C for 1 h, the depression, together with the preceding anodic hump became more pronounced and preserved for longer times (even for three cycles). Because these effects result from the increased amounts of lower chromium oxides and the enhanced structural disordering, it is likely that some part of the intercalate becomes more firmly bonded within the graphite pockets and new structural traps encapsulating intercalate are formed on heating. In consequence, intercalation of H<sub>2</sub>SO<sub>4</sub> into a new system of increased energy bonding requires a higher positive potential. The presence of the effects in the potentiodynamic curves of the original compound, marked A1-W1, becomes clear in the light of the fact that this GIC of disordered structure is synthesized at 200°C [8, 9]. The proposed mechanism also accounts for the results obtained for sample A2-AC. The worsening of structural ordering, observed after this compound is heated at 160°C (Fig. 2(b) and (c)), leads to the appearance of the same features on the potentiodynamic curves (Fig. 5) as those recorded for the pristine sample A1-W1. These effects increase on prolonging the time of heat treatment.

In conclusion, this work yields definitive evidence that the cathodic jump phenomenon recorded on the potentiodynamic curves during the subsequent intercalation of sulphuric acid into pristine CrO<sub>3</sub>-GIC is associated with the reaction occurring between the cointercalating H<sub>2</sub>SO<sub>4</sub> and the chromium trioxide and/or lower chromium oxide primarily intercalated in graphite. To approach the problem of interaction between sulphuric acid and CrO<sub>3</sub>-GICs *in situ*

X-ray measurements are necessary in the future. The potentiodynamic technique, involving the thermal modification of CrO<sub>3</sub>-GICs, is not only a new analytical method of sensitivity exceeding that of X-ray analysis, but may also serve as a useful tool for selection of proper CrO<sub>3</sub>-GICs for practical use, especially as cathode materials for chemical power sources.

#### Acknowledgements

Financial support of this work by the State Committee for Scientific Research of Poland (KBN grant 3 0074 91 01) is gratefully acknowledged.

#### References

- [1] U. Hofmann and A. Frenzel, *Z. Elektrochem.* **37** (1931) 613.
- [2] H. Thiele, *Z. anorg. allg. Chem.* **206** (1932) 407.
- [3] N. Iwashita and M. Inagaki, *Synth. Met.* **34** (1989) 139.
- [4] M. Inagaki, N. Iwashita and E. Kouno, *Carbon* **28** (1990) 49.
- [5] J. M. Skowroński and K. Jurewicz, *Synth. Met.* **40** (1991) 161.
- [6] J. M. Skowroński, J. Douglade and A. Metrot, in 'Materials Science Forum' (edited by D. Tchoubar and J. Conard), Vols. 91-93, Trans. Tech Publications, Zürich (1992), pp. 659-664.
- [7] N. Platzer and de la Martinière, *Bull. Soc. Chim. France* **197** (1961).
- [8] J.M. Skowroński, *Electrochim. Acta* **30** (1985) 989.
- [9] *Idem*, *Carbon* **24** (1986) 185.
- [10] *Idem*, *Synth. Met.* **22** (1987) 157.
- [11] *Idem*, *Carbon* **27** (1989) 537.
- [12] J. M. Skowroński and K. Jurewicz, *J. Appl. Electrochem.* **22** (1992) 535.
- [13] B. Kubota, *J. Am. Ceram. Soc.* **44** (1961) 239.
- [14] L. B. Ebert, R. A. Huggins and J. I. Brauman, *Carbon* **12** (1974) 199.
- [15] J. G. Hooley and M. Reimer, *ibid.* **13** (1975) 401.
- [16] W. Metz and H. Meyer-Spasche, *Synth. Met.* **1** (1979/80) 53.
- [17] J. M. Skowroński, *J. Thermal Anal.* **34** (1988) 989.
- [18] *Idem*, *Carbon* **26** (1988) 613.
- [19] T. Kobayashi, H. Kurata and Uyeda, N., *J. Phys. Chem.* **90** (1986) 2231.
- [20] J. M. Skowroński, *Synth. Met.* **55-57** (1993) 1447.
- [21] J. O. Besenhard, E. Wudy, H. Möhwald, J. J. Nickl, W. Biberacher and W. Foag, *ibid.* **7** (1983) 185.
- [22] A. Metrot and H. Fuzellier, *Carbon* **22** (1984) 131.
- [23] H. Shioyama and R. Fuji, *ibid.* **25** (1987) 771.
- [24] J. M. Skowroński, *Electrochim. Acta* **32** (1987) 1285.
- [25] *Idem*, *ibid.* **33** (1988) 953.
- [26] L. B. Ebert and J. C. Scanlon, *Carbon* **25** (1987) 437.
- [27] *Idem*, *ibid.* **28** (1990) 253.