

THE INFLUENCE OF A CrO_3 -GRAPHITE INTERCALATION COMPOUND ON THE DISCHARGE CHARACTERISTICS OF AN MnO_2 CATHODE IN ALKALINE ELECTROLYTE

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Summary

The paper provides experimental data demonstrating the positive effect which a graphite/chromium trioxide (CrO_3 -GIC) intercalation compound has on the cathodic performance of manganese dioxide in alkaline electrolyte. The increased cathode capacity of the mixed cathodes is explained in terms of reduction reactions of CrO_3 -GIC. The galvanostatic and potentiodynamic curves are used to discuss the changes occurring in the structure of CrO_3 -GIC during discharge.

1. Introduction

Manganese dioxide is mixed with carbon materials such as carbon black, coke and/or graphite to improve its electrical conductivity. The cathode-active material for alkaline cells is mainly blended with graphite particles. The intercalation of graphite by various elements or molecules produces graphite intercalation compounds (GICs) having new physical as well as chemical properties. GICs contain intercalant between adjacent layers of graphite. The concentration of intercalant is related to the stage number, *i.e.*, the number of graphite layers separating two layers of intercalant, the method of intercalation, the kind of graphite, and the particular intercalant. GICs can be a one-phase reservoir of electrochemically active substance for primary cells or can undergo reversible electrochemical intercalation-deintercalation processes serving as attractive substances for secondary cells. The graphite intercalation compounds with chromium trioxide (CrO_3 -GICs) contain a high oxidation state intercalant. Contrasting with free CrO_3 which dissolves easily, even in cold water, the intercalated oxide is entirely resistant to acid solutions [1 - 3] and is only slightly soluble in alkaline electrolytes [5]. The capacities of the mixed cathodes composed of MnO_2 and CrO_3 -GICs have been reported to be higher than MnO_2 -graphite cathodes operating in NH_4Cl solution [5].

To date, the application of graphite intercalation compounds in alkaline electrolytes has been confined to the cathodes converted from GICs with MnCl_2 and NiCl_2 [6 - 8]. The present paper gives preliminary results on the influence which a CrO_3 /graphite intercalation compound has on the performance of an MnO_2 cathode in 7 M KOH.

2. Experimental

2.1. Materials and preparation

The manganese dioxide used in this work was International Common Sample I. C. No. 1 which is electrolytic $\gamma\text{-MnO}_2$ made by a titanium anode. 9900 spectrographic graphite flakes of diameter smaller than 25 μm provided by La Carbone-Lorraine (France) were used to increase the electrical conductivity of the cathode. The same graphite was used to prepare the intercalation compound with CrO_3 . Reagent grade chromium trioxide produced by POCH Gliwice (Poland) was used without further purification. The dry method of intercalation involved heating CrO_3 /graphite (5:1 by weight) mixture in air at 200 °C for 5 h. The product was then purified using the procedure described earlier [1, 2]. To remove unreacted CrO_3 the product was initially treated with boiling water and then with 6 M HCl at 100 °C: treatment with acid allows the removal of a physical admixture of lower chromium oxides formed due to side reactions occurring during the intercalation [9]. Finally, washing with boiling water was continued until the Cr^{6+} ion concentration in the filtrate was lower than $5 \times 10^{-2} \mu\text{g cm}^{-3}$. The purified product, denoted F1-S1, was chemically analysed and the C/Cr ratio (13.6) determined. X-ray diffraction data obtained from a sample of the F1-S1 using Ni-filtered Cu $K\alpha$ radiation revealed diminution of the intensity of the peaks corresponding to pure graphite, and the appearance of a new peak at 3.60 Å. This peak had a greater intensity than the remaining graphite peak. The presence of this new peak confirmed intercalation since, on heating the compound above 220 °C, the peak disappeared whereas the initial graphite peaks increased again in intensity. It is consistent with the evidence that above 220 °C the decomposition of free [10], as well as of intercalated, CrO_3 [9, 11] takes place. Evidence, arising from the X-ray method, for the intercalation of graphite with CrO_3 by the dry method, as well as from other methods, is discussed elsewhere [12].

2.2. Measurements

The construction of the experimental cell used in the present work was, in general, the same as that described by Fernandes *et al.* [13]. The cathode mix was pressed into a cylindrical Teflon cap (inner dia. 20 mm), which had a Luggin capillary in its wall and a platinum spiral current collector at the bottom. The cathode was kept in place by a polypropylene fibre and a perforated Teflon disc. After the cathode had been mounted in place this part of the cell was screwed into a cylinder containing the electrolyte. The

platinum net counter electrode was mounted in the upper section of this part of the cell. The cathode mix was dipped, under vacuum, into 15 cm³ of 7 M KOH (unless otherwise noted) and the Luggin capillary, filled with the electrolyte under investigation, was fitted to the Hg/HgO reference electrode. The cathode mix consisted of 100 mg of MnO₂ and 1 g of graphite material (either pure graphite or a mix of pure graphite with graphite intercalation compound) (Table 1). The cell was continuously discharged at a stabilised current of 1 mA for 8 h and the voltage drop (closed circuit voltage (CCV)) was recorded. The cell was then left on open-circuit for 17 h to obtain the open-circuit voltage (OCV) after 8 mA h discharge. This regime of 8 h discharge at 1 mA followed by a 17 h rest period was continued until the final voltage of -0.4 V was reached. After a subsequent rest period the final OCV was noted. To gain insight into the cathode processes taking place within the intercalation compound measurements using both pure graphite and CrO₃-GIC electrodes were also carried out. Because some of the intercalant may be enclosed in the graphite pockets [4] these electrodes were discharged at the lower current of 0.2 mA. In this way a better utilization of the intercalant capacity was expected. In addition, for the same electrodes, potentiodynamic curves were recorded. Runs with a scan rate of 0.25 mV s⁻¹ were initiated at the rest potential of the electrode and polarization was continued in the cathodic direction until a potential of -0.8 V *versus* the Hg/HgO reference electrode was reached. All measurements were performed at a temperature of 20 °C. Four series were made for each electrode and the reproduceability was satisfactory. The average characteristics are presented here.

TABLE 1

Influence of graphite intercalation compound on discharge characteristics of manganese dioxide in 7 M KOH at 1 mA

Cathode No.	Composition (g)	OCV initial (mV)	CCV after 8 mA h (mV)	OCV after 8 mA h (mV)	Polarization (mV)			Discharge capacity up to -0.4 V (mA h)
					8 mA h	16 mA h	24 mA h	
1	γ -MnO ₂ = 0.1 g Graphite = 1.0 g	245	-41	10	51	44	48	27.4
2	γ -MnO ₂ = 0.1 g Graphite = 0.7 g CrO ₃ -GIC = 0.3 g	280	-78	-22	56	47	44	30.8
3	γ -MnO ₂ = 0.1 g Graphite = 0.4 g CrO ₃ -GIC = 0.6 g	303	5	51	46	34	41	31.8

3. Results and discussion

In the previous paper [4] it was shown that the graphite/ CrO_3 intercalation compound prepared by the dry method was much less sensitive to alkaline deintercalation than was the compound prepared by the solvent method. The latter appeared to be readily deintercalated on immersion in an alkaline solution. Most of the intercalant was leached out over several hours. It has been suggested that the ionic properties, the composition of intercalated species, and the structural cramps within the intercalated layers are responsible for the different behaviours of the compounds of each method. The compound used in the present work belongs to the dry method category. Knowledge of the alkaline deintercalation of these compounds [4] allowed us to anticipate that the amount of chromium dissolved in concentrated KOH would not exceed 0.1% of the total chromium content. In manufacturing the electrodes the dissolution of the intercalated oxide released under pressure was also taken into consideration. It has been shown [1, 2, 4] that the disruption of the intercalated flakes of graphite by pressure and/or milling makes deintercalation easier. Chemical analysis revealed, however, that the amount of chromium leached out from the compressed cathodes was negligible. This made it possible to prepare the experimental cathodes in the compacted form. The contribution of the dissolved hexavalent chromium to the capacity increase resulting from admixing CrO_3 -GIC with the manganese dioxide cathode is considered below.

Figure 1 shows the influence of the graphite intercalation compound on the performance of MnO_2 /graphite cathodes. It can be seen that they all demonstrate the typical 'S-shape' polarization curves characteristic of homogeneous (single phase) reduction of $\gamma\text{-MnO}_2$ [14]. The better discharge

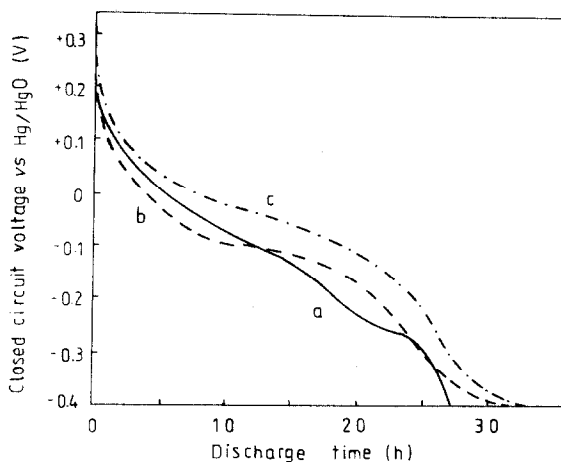


Fig. 1. Discharge curves obtained in 7 M KOH at 1 mA for: a, cathode 1, 0.1 g $\gamma\text{-MnO}_2$ + 1.0 g graphite; b, cathode 2, 0.1 g $\gamma\text{-MnO}_2$ + 0.7 g graphite + 0.3 g CrO_3 -GIC, c, cathode 3, 0.1 g $\gamma\text{-MnO}_2$ + 0.4 g graphite + 0.6 g CrO_3 -GIC.

performance of cathode 3, which contains 0.6 g of intercalation compound (60% pure graphite substituted), compared with cathode 1, free from CrO_3 -GIC, is especially pronounced. The presence of the intercalation compound causes the increase in the OCV. It can be effected not only by CrO_3 inserted within the graphite structure but also by the presence of the de-intercalated chromate ions in the electrolyte. As can be seen from Table 1 the polarization values of all cathodes are similar. A small increase in the polarization of cathode 2 at 8 mA h corresponds to lowering the discharge curve below that of a $\gamma\text{-MnO}_2$ cathode. Chemical analysis of the electrolyte made after finishing the discharge yielded the following results: for the electrolyte of cathode 2 the average amounts of the Cr^{6+} and Cr^{3+} ions were $3.1 \mu\text{g}$ and $114.0 \mu\text{g}$, respectively, whereas for the electrolyte of cathode 3 the given values were $6.9 \mu\text{g}$ and $248.6 \mu\text{g}$, respectively. If we assume that all trivalent chromium (for example as $\text{Cr}(\text{OH})_3$) was formed due to the reduction of chromate ions leached from the intercalation compound, then the capacity corresponding to the 3 electron reduction can be calculated. The discharge times obtained at 1 mA for the 100% reaction efficiency are 10.6 min for cathode 2 and 23.0 min for cathode 3. These values are very small compared with the increased discharge capacities effected by the presence of CrO_3 -GIC in the cathode mix (Table 1, Fig. 1). It suggests that the reactions occurring within the intercalation compound are mainly responsible for the improvement in the cathode performance. It is reasonable at this point to acknowledge that a portion of the trivalent chromium present in the electrolyte can also originate from dissolving chromic hydroxide (or hydrated chromic oxide) [15] formed between the graphite interspaces due to the reduction of the intercalant.

To verify the hypothesis that the reduction takes place within the graphite structure, measurements with MnO_2 free electrodes were undertaken. Figure 2 shows the discharge curves obtained at 0.2 mA. Very sharp potential peaks are observed on curve 'a' representing the electrode which includes 0.3 g of CrO_3 -GIC (the proportion used for cathode 2). If the electrode includes double the intercalation compound (the same amount as used in cathode 3) no peaks are visible up to -0.4 V (curve b). In this case a broad wave appears at about -0.45 V which precedes the violently oscillating potential changes which occur in the range -0.47 to -0.55 V. It must be emphasized that at these potentials hydrogen evolution did not occur.

These curious phenomena have also been observed during discharge of the compacted as well as the powder electrodes made from the same compound as that used here but without admixed pure graphite [16]. On the other hand, typical discharge curves without any potential oscillations were observed for pure graphite in the KOH solution containing chromate ions. These results indicate that the sudden potential rise is not caused by either the pressure effect or the reduction of chromate ions at the graphite flakes' surface.

The reason should be sought in the changes occurring within the intercalated layers of graphite as a result of the reduction process. From the

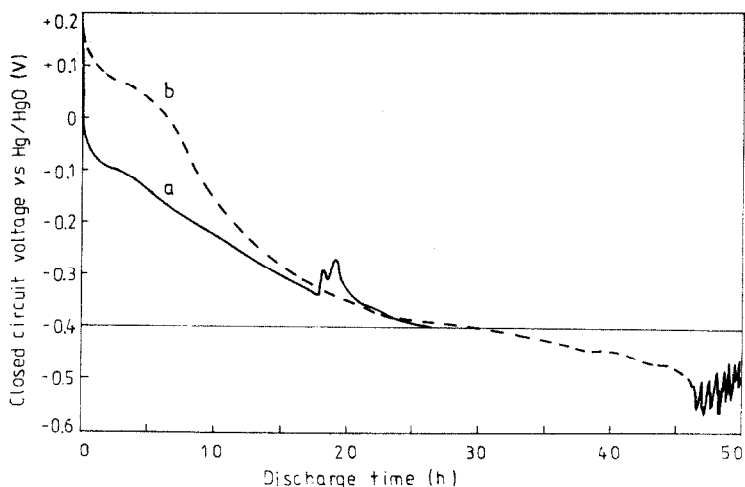


Fig. 2. Discharge curves obtained at 0.2 mA for the following electrodes: a, pure graphite (0.7 g) + CrO_3 -GIC (0.3 g) in 7 M KOH (OCV = 177 mV); b, pure graphite (0.4 g) + CrO_3 -GIC (0.6 g) in 7 M KOH (OCV = 188 mV).

thermodynamic data [15] it is likely that during the reduction reactions the intercalant is converted to chromic hydroxide. 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 surface area. In such a case the current density decreases. On the other hand, exfoliation, through the disruption of graphite pockets, facilitates the diffusion of electrolyte into the graphite and allows the molecules of intercalant previously blocked to take part in the reaction. In this way, the increased concentration of chromates formed within the graphite could be the next reason for the potential rise.

The differences in the potentials at which the oscillations on curves 'a' and 'b' of Fig. 2 appear may arise from the fact that the current relative to the amount of the intercalation compound contained in electrode 'a' is double that of electrode 'b'. The other reason may lie in the different amount of pure graphite separating the particles of CrO_3 -GIC. Perhaps these factors make the reduction process occurring in electrode 'b' more uniform and gradual. To what extent the intercalation compound deteriorates during discharge needs to be determined by separate experiments. In this work we undertook to test whether the suggested discharge mechanism is plausible.

The potentiodynamic curves recorded for the graphite/ CrO_3 -GIC cathodes (Fig. 3 'a' and 'b')* show that the cathodic currents begin to increase as the potential becomes more and more negative and attain maxima at -570 and -645 mV, respectively. Obviously, the current values are

*Note the different scale for each of the 3 curves.

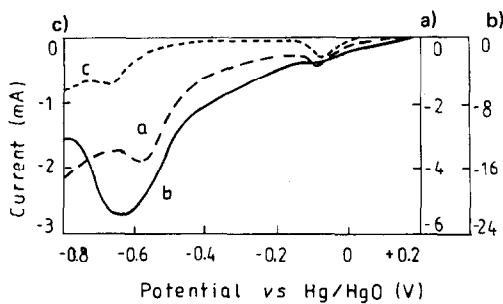


Fig. 3. Potentiodynamic curves obtained for the following electrodes: a, pure graphite (0.7 g) + CrO_3 -GIC (0.3 g) in 7 M KOH; b, pure graphite (0.4 g) + CrO_3 -GIC (0.6 g) in 7 M KOH; c, pure graphite (1.0 g) in 7 M KOH + 0.01 M K_2CrO_4 , scan rate: 15 mV min^{-1} .

greater for the electrode containing the higher concentration of CrO_3 -GIC (curve b). The very broad potential reaction region can be associated with different degrees of accessibility of the intercalant depending on the structural constraints. It was ascertained that the slight peak at about -100 mV originates from pure graphite and can be associated with the reduction of oxygen adsorbed on the particle surfaces. It is clearly seen that the beginning of the current increase on the potentiodynamic curve recorded for pure graphite in 7 M KOH + 0.01 M K_2CrO_4 (curve c in Fig. 3) takes place at more negative potentials than in curves a and b. The peak at -666 mV is also much smaller*. It is worth noting that the chromate ion concentration used is about one order of magnitude greater than the maximum concentration of chromium found in electrolytes after the discharge of $\text{MnO}_2/\text{CrO}_3$ -GIC (cathodes 2 and 3). Because the solubility of chromic hydroxide is appreciably degraded as the pH of the solution decreases [15], the structure distortion of CrO_3 -GIC due to the formation of the reduction product should be greater in more dilute electrolyte. The potentiodynamic curves obtained in 0.1 N KOH [16] confirm this assumption.

4. Conclusions

(i) The present paper provides the experimental data that demonstrate the positive effect of the graphite intercalation compound with chromium trioxide on the performance of manganese dioxide in alkaline electrolyte.

(ii) It is shown that although the reduction reactions proceeding inside the intercalation compound are the major contributors to improvements in the discharge capacity of MnO_2 , nevertheless some charge can also be gained due to the reduction of chromates occurring at the surface of the graphite flakes.

(iii) Because many problems still remain, further investigations are needed. Studies on the electrochemical and structural changes in CrO_3 -GIC

*Note the different scale for each of the 3 curves.

due to the reduction in alkaline solutions have already been undertaken in our laboratory. From a practical point of view it will be interesting to evaluate the changes in the kinetics of the discharge of manganese dioxide effected by the reactions of the graphite intercalation compound. Also, the self-discharge of the cathode mix needs to be determined. To obtain data of technological importance, further experimental investigations using intercalation compounds of different composition and structure will be undertaken.

Acknowledgements

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