

SHORT COMMUNICATION

Improvement of the discharge capacity of the alkaline MnO_2 -Zn cell by using graphite intercalation compounds with CrO_3

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1. Introduction

Graphite intercalation compounds with chromium trioxide (CrO_3 -GICs) contain the intercalated material in a high oxidized state between the graphite layers. In contrast to free CrO_3 , the intercalated oxide is entirely resistant to acid solutions [1–4] and in alkaline electrolytes its dissolution is also slight [5]. Based on potentiodynamic measurements, it has been reported earlier [1, 2, 4] that CrO_3 -GICs demonstrate electrochemically active redox reactions in acid aqueous electrolytes. Studies with NH_4Cl solutions showed that the capacities of mixed cathodes composed of MnO_2 and CrO_3 -GICs, appear to be higher than those of MnO_2 -graphite cathodes [3]. Up to the present, the application of graphite intercalation compounds in alkaline electrolytes has been limited to cathodes formed from graphite with MnCl_2 and NiCl_2 [6–8]. This paper presents preliminary results on the performance of CrO_3 -GICs in experimental alkaline MnO_2 -Zn cells.

2. Experimental details

CrO_3 -GICs were prepared from purified Caucasian graphite flakes (Soviet Union), using the 'dry' method described by Hooley and Reimer [9], and the 'impregnation-dry' method discussed previously in detail [1, 2]. Reagent grade CrO_3 , produced by POCH Gliwice (Poland), was used without further purification. Chemical analysis data of the used graphite and CrO_3 -GICs are listed in Table 1. The cathode mix was prepared by mixing the graphite compounds with battery-grade, electrolytic γ - MnO_2 (Tekkosha, Japan). The weight of the cathode mix was always 200 mg. The experimental cell used to determine the discharge characteristics was made in the following way. The anode cup (inner diameter 18 mm, height 8 mm) was formed by electroplating porous zinc from a zincate solution onto a copper cup [10]. The anode was then chemically amalgamated using mercuric chloride solution acidified with HCl . The content of mercury in the anodes ranged between 0.71 and 0.78 wt %. All anodes were prepared in the same manner. The anode capacity was in great excess with respect to the cathode mix capacity. The inner surface of the anode was lined with a Nylon separator and the cathode mix, composed of MnO_2 , CrO_3 -GIC and/or graphite, was placed into the zinc cup and moistened with 0.2 cm^3 of electrolyte (7 N KOH). Then the drilled

Table 1. Preparation and chemical analysis of graphite intercalation compounds

Sample	Intercalation method	Formula ¹
CD	Purified to 99.7 wt % C, Caucasian graphite containing 87 wt % C, flakes smaller in diameter than $170\text{ }\mu\text{m}$	
CD1-S1	'Dry' method [9]	$\text{C}_{57}\text{CrO}_3$
CD1-W1	'Impregnation-dry' method [2]	$\text{C}_{52}\text{CrO}_3$

¹ Intercalant is assumed to be CrO_3 only.

graphite rod was fitted into the cup and pressed, using a pressure of 5 MPa. A relatively low pressure was applied to avoid deterioration of the intercalation compounds [2]. A narrow canal in the graphite rod, serving as venting duct, also allowed the final portion of electrolyte of about 0.5 cm^3 to be poured into the cell. Excess electrolyte was allowed to flow through a hole in the anode wall. The cell was under zero current flow for 0.5 h and then the discharge was initiated. The cell was continuously discharged, by passing currents of 5, 3, or 0.5 mA, until the end voltage of 0.7 V was reached. All measurements were carried out at 20°C . For a given cathode composition, three discharge runs were carried out. The differences in the cell capacities did not exceed 3%. Figures 1–3 display the average recordings.

3. Results and discussion

The influence of the intercalation compound on the discharge characteristics of the alkaline MnO_2 -Zn cell was determined by using the cathode compositions as in previous work [3] (Table 2). From this table it is seen that the open circuit voltages (OCV) of the cells containing CrO_3 -GIC in their cathodes are somewhat higher than those of cells free of GIC. Figure 1 shows that the discharge time at a current of 5 mA increases if 25 wt % graphite in the cathode mixture is replaced by the same weight of CrO_3 -GIC. As can be seen from this figure, the voltage drop of the cell containing sample CD1-S1 (dry method product (curve 2)) is up to 0.8 V lower than that with sample CD1-W1 (impregnation-dry method product (curve 3)). This is striking because sample CD1-S1 contains a somewhat smaller concentration of the intercalant as compared with sample CD1-W1 (Table

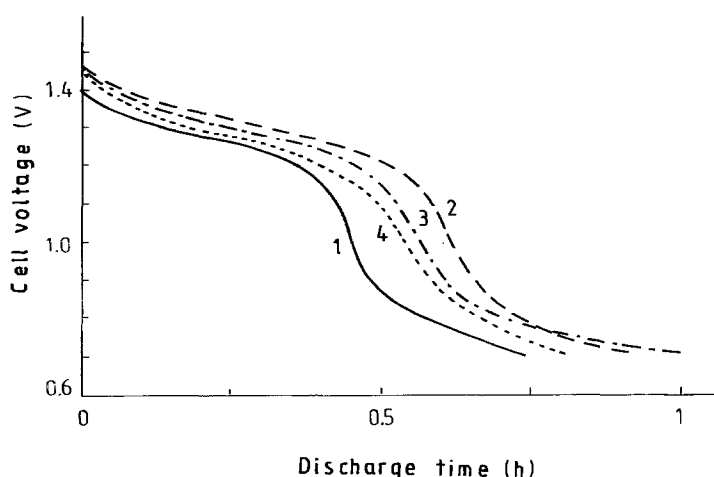


Fig. 1. Discharge curves obtained in 7 N KOH at 5 mA for cells with different cathodes: (1) 50% MnO_2 + 50% CD; (2) 50% MnO_2 + 25% CD + 25% CD1-S1; (3) 50% MnO_2 + 25% CD + 25% CD1-W1; (4) 50% MnO_2 + 50% CD1-W1.

1). This behaviour could possibly be explained by differences existing in the chemical nature of the intercalant and the structure of CrO_3 -GICs. It has been reported previously [1, 2, 4, 5] that CrO_3 -GICs contain not only the intercalated CrO_3 but also chromium oxides of lower oxidation state, such as Cr_2O_3 and/or Cr_2O_5 . Electrochemical analysis of various samples of CrO_3 -GICs showed the amount of lower chromium oxides to be smaller than 1% of the total content of chromium [5, 11]. It may be assumed that, because of the increased activity of the graphite edges, the formation of these oxides during the intercalation reaction between molten CrO_3 and graphite took place preferentially at the periphery of the graphite layers and that the oxides formed may possibly hinder the access of electrolyte to the inner regions of the graphite [5]. As reported previously [1, 2, 4] sample CD1-W1 contains more lower chromium oxides than sample CD1-S1. According to this, the greater slope in curve 3 of Fig. 1 (representing sample CD1-W1), in comparison with curve 2 (sample CD1-S1), may be due to the increased diffusion polarization resulting in the inhibition of reaction of the intercalant enclosed within the graphite layers. This explanation is likely because, upon discharging under decreased currents

of 3 or 0.5 mA (Figs 2 and 3), the increase in the discharge capacity coincides better with the intercalant content. As seen from Figs 2 and 3 the discharge capacity is greater for the sample CD1-W1, which contains a higher total amount of chromium, and a distinctly higher amount of electrochemically active lower chromium oxides [1, 4, 5]. The discharge time recorded for the cell free of CrO_3 -GIC shows that only a small part of the theoretical capacity of MnO_2 (reduction of Mn(IV) to Mn(III)) is being utilized if the discharge is carried out at excessively high current. For example, in the case of cell 1, discharged at 3 mA (curve 1 of Fig. 2), this value is about 20%. Such low efficiency may possibly be caused by resistance and diffusion polarization resulting from the cell construction. This suggestion seems to be plausible because the practical capacity of the cell distinctly increases (by a factor of approximately 3) when the discharge is carried out at much lower current of 0.5 mA (curve 1 of Fig. 3). As seen from Fig 3, the increase in the discharge capacity of cells effected by the presence of CrO_3 -GICs in the cathode mix is most pronounced for cell 3 (sample CD1-W1) in its final period of discharge.

In the present work we attempted to determine to what extent the increase in the discharge capacity could result from a homogeneous reduction of chromate ions possibly present in the electrolyte, due to dissolution and pressure deintercalation. Chemical analyses of electrolyte samples taken from the cells before the discharge tests were carried out. They showed the total amount of chromate ions to be always smaller than $2 \mu\text{g Cr(VI)}$. The theoretical

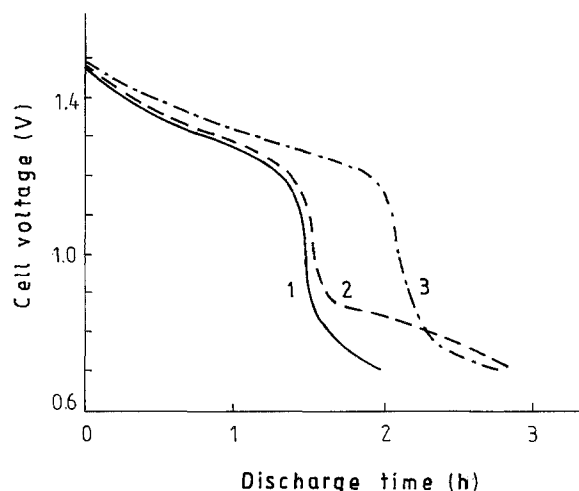


Fig. 2. Discharge curves obtained in 7 N KOH at 3 mA for cells with different cathodes: (1) 50% MnO_2 + 50% CD; (2) 50% MnO_2 + 25% CD + 25% CD1-S1; (3) 50% MnO_2 + 25% CD + 25% CD1-W1.

Table 2. Composition of cathode mixtures and open circuit voltages of cells

Cell No.	Composition of cathode (wt %)				OCV (V)
	$\gamma\text{-MnO}_2$	CD	CD1-S1	CD1-W1	
1	50	50	—	—	1.523
2	50	25	25	—	1.533
3	50	25	—	25	1.548
4	50	—	—	50	1.539

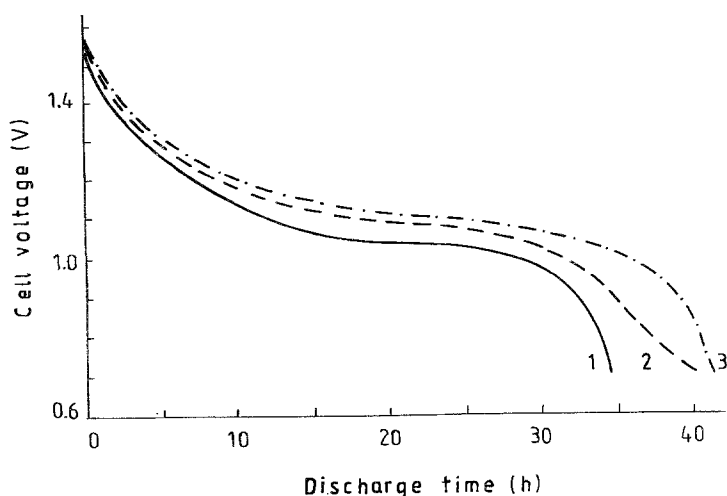


Fig. 3. Discharge curves obtained in 7 N KOH at 0.5 mA for cells with different cathodes: (1) 50% MnO_2 + 50% CD; (2) 50% MnO_2 + 25% CD + 25% CD1-S1; (3) 50% MnO_2 + 25% CD + 25% CD1-W1.

capacity assuming a 3-electron reduction of Cr(VI) would only amount to about 11 mA s. Obviously this cannot account for the capacity increase of the cell observed in the presence of CrO_3 -GICs in the cathode mix. Because of the fact that no X-ray lines associated with the presence of graphitic oxide have been found for CrO_3 -GICs [2] the results obtained in the present work suggest that reduction reactions of chromium oxides occurring in the solid CrO_3 -GIC cathode should be responsible for the improvement of the characteristics of the cells. The theoretical capacities calculated by assuming that all intercalant exists exclusively in the form of CrO_3 and upon discharging chromium trioxide is completely reduced to Cr_2O_3 are equal to 5.1 and 5.6 mAh for the cathodes containing samples CD1-S1 and CD1-W1, respectively. If we assume that the capacity increases, obtained with respect to the capacity of the cell with the cathode free of CrO_3 -GIC (Fig. 3), result from the mentioned reaction of the intercalant, then the reduction efficiency of CrO_3 -GICs present in the cathode mix would be about 55% for sample CD1-S1 (curve 2) and 59% for sample CD1-W1 (curve 3). Obviously, the values obtained are very rough because the calculations do not take into consideration the effects resulting from the presence of lower chromium oxides and the possibility that some fraction of intercalant, if tightly enclosed within the graphite pockets, could not participate in electrochemical reaction [5].

Although there is, at present, no experimental evidence for the interaction between MnO_2 and CrO_3 -GICs, such a possibility seems to us to be worthy of investigation. In order to investigate this problem more exhaustively, studies on $\text{MnO}_2/\text{CrO}_3$ -GIC cathodes, including much more concentrated CrO_3 -GIC prepared from very fine graphite flakes, have been carried out more recently [12]. It should be recalled at this point that CrO_3 -GICs have electrical resistivities somewhat higher than those of graphite [13]. This fact may explain why the characteristics of cells, in which all graphite is replaced by GIC, become worse. It is apparent from Fig. 1 that curve 4, referring to a cell in which all the graphite was completely replaced by

CrO_3 -GIC, shows a higher capacity than curve 1, for a cell in which the cathode did not contain an intercalation compound.

The present work showed that, similarly to the results for CrO_3 -GICs in Leclanché-type cathodes [3], the intercalation compounds also appear to have a positive effect on the performance of alkaline MnO_2 -Zn cells. We realize that the construction of our experimental cell is inferior to that of commercial cells. However, fabrication of commercial-type cells would require large amounts of the intercalation compounds. Nevertheless, using comparable conditions to simulate battery performance, we have been able to ascertain the effect of CrO_3 -GICs on the performance of manganese dioxide-zinc systems. The results obtained prompted us to direct further studies towards the mechanism of the $\text{MnO}_2/\text{CrO}_3$ -GIC cathode reactions. Understanding of these reactions will allow the formulation of a cathode suitable for use in a commercial cell.

Acknowledgements

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