

THE MOLYBDENUM TRIOXIDE DOPED MANGANESE DIOXIDE ELECTRODE: 1. USE AS LOW TEMPERATURE BATTERY CATHODES*

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Summary

A study of the chemical and electrochemical properties of manganese dioxide cathodes containing molybdenum trioxide is described. The manganese dioxide was made by the decomposition of a dissolved mixture of manganous nitrate and a small quantity of molybdenum trioxide.

It was found that the chemical composition of the manganese dioxide was affected by the presence of less than 1% molybdenum trioxide. In certain cases, considerable improvement was observed in the discharge behaviour of electrodes made with these oxides. The doped cathodes were assessed in the $Zn/H_2SO_4/MnO_2$ reserve-primary system.

Résumé

Nous décrivons une étude faite sur les propriétés chimiques et électrochimiques des cathodes de bioxyde de manganèse contenant du trioxyde de molybdène. Le bioxyde de manganèse avait été préparé par la décomposition d'un mélange dissous de nitrate de manganèse et d'une quantité minime de trioxyde de molybdène.

Il a été constaté que la composition chimique du bioxyde de manganèse était affectée quand il y avait présence de trioxyde de molybdène à moins de 1%, et dans certains cas, nous avons remarqué une amélioration considérable dans le comportement de décharge d'électrodes fabriquées avec ces oxydes. Les cathodes dopées ont été évaluées en utilisant le système réserve-primaire, $Zn/H_2SO_4/MnO_2$, C.

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Introduction

In previous work on manganese dioxide cathodes in sulfuric acid [1], the low temperature behaviour of the electrode was found to be not as satisfactory as might be desired.

This unsatisfactory behaviour is thought to be due to a combination of slow dissolution of reaction products and slow diffusion of hydrogen ions in the interior of the oxide. Only a small fraction of the oxide near the surface is therefore reduced, and low utilization of the electrode results. It was thought that by introducing small amounts of foreign ions, such as Mo^{6+} , into the dioxide, an increase in the diffusion rate might be expected, and higher utilization might occur.

The molybdenum-doped manganese dioxide in this work was made by decomposing a solution of manganese nitrate containing molybdenum trioxide. The experimental work is divided into two main sections: (1) establishment of the conditions for forming oxides with different compositions and determination of the constituents in them; and (2) discharge of the electrodes made from the oxides and correlation of the discharge characteristics with the composition.

Experimental and results

Oxide preparation

The oxide was made by decomposing 35.8 g of a 50% manganous nitrate solution (corresponding to 0.1 mol manganous ions) containing different amounts of molybdenum trioxide. Two different decomposition temperatures were used (135 °C and 180 °C). The time of decomposition was five days. After decomposition, the oxide was ground to pass 60 mesh. The powder was added to 20 ml of 50% ammonia solution and stirred for 30 min. This removed unreacted molybdenum as ammonium molybdate and precipitated unoxidized manganous ions as manganous hydroxide. After washing first with 50% ammonia solution and then with distilled water, the powder was dried to constant weight.

To determine the constituents of the oxide, a small amount of the oxide was dissolved in a mixture of sulfuric acid and oxalic acid and analyzed.

Molybdenum in the oxide as a function of the molybdenum trioxide in the manganous nitrate solution

The molybdenum was determined spectrophotometrically with thiocyanate [2]. The results, which are shown in Fig. 1, show that the amount of molybdenum that goes into the oxide increases with increasing amount of molybdenum trioxide in the manganous nitrate solution and also with increasing temperature. However, a maximum level is reached, most noticeably at 135 °C. Whether this maximum level is constant or changes with the time of decomposition has not been determined.

For 135 °C the maximum level is near 10^{-2} mol molybdenum per mole manganese. The mole ratio is above 2×10^{-2} at 180 °C.

Available oxygen in the oxide as a function of the molybdenum trioxide in the manganous nitrate solution

In order to determine the available oxygen in the oxide, it was necessary to determine both the total amount of manganese in the sulfuric acid-oxalic acid solution and the amount of the oxalic acid used when the oxide was dissolved. The manganese was determined by adding some of the solution to a strong sodium pyrophosphate solution and titrating with a permanganate solution [3]. The oxalic acid used during the dissolution was determined by titrating the remaining oxalic acid with permanganate [4].

A blank determination was made in which only molybdenum trioxide was dissolved in the oxalate solution. Titration showed that no oxalate was used in the dissolution process. The molybdenum ions therefore do not interfere in the analysis.

The results, given in Fig. 2, show that the amount of available oxygen decreases towards a limit with increasing amounts of molybdenum trioxide in the manganous nitrate solution. The limit also decreases with increasing temperature. With a decomposition temperature of 135 °C the limit is 1.948 (expressed as x in MnO_x). The limit is 1.936 when 180 °C is used as a decomposition temperature.

If the results in Fig. 1 are compared with the results in Fig. 2, it appears that there is a connection between the amount of molybdenum in the oxide and the amount of available oxygen. For either temperature, the higher the molybdenum content of the oxide the lower the amount of available oxygen. This indicates that the molybdenum that goes into the oxide binds a certain amount of oxygen and renders it unavailable. However, the ratio of bound oxygen to molybdenum is lower for the oxide produced at 180 °C than that produced at 135 °C. This may be an ageing effect, accelerated at the higher temperature.

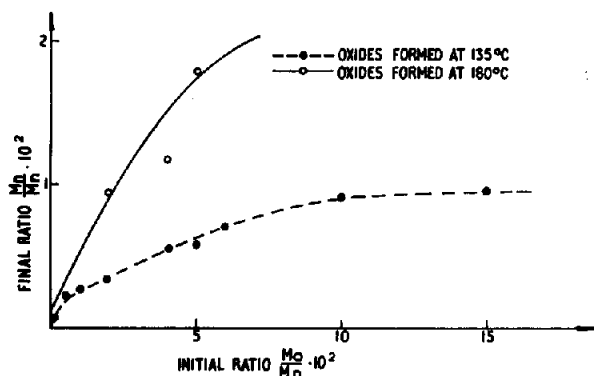


Fig. 1. Fraction of molybdenum in the oxide as a function of the initial fraction in the manganous nitrate solution.

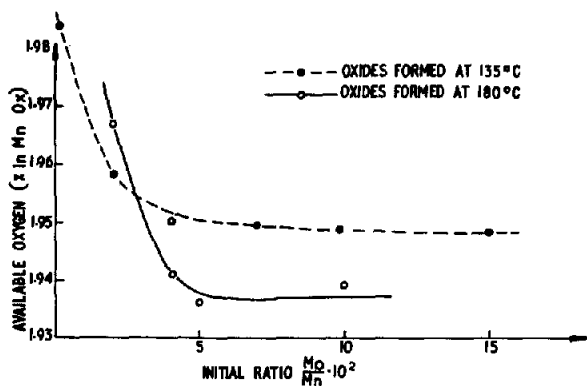


Fig. 2. Available oxygen in the oxide as a function of the initial atom ratio Mo/Mn in the manganous nitrate solution.

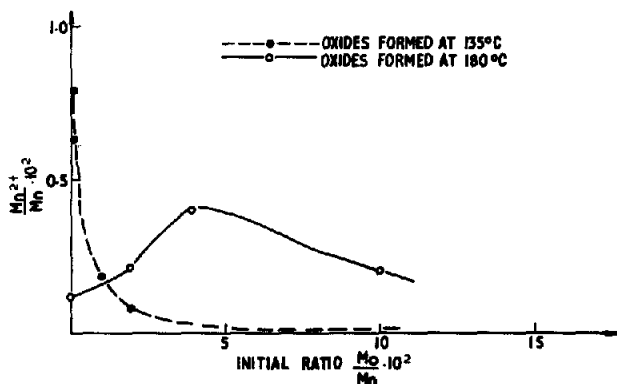


Fig. 3. Fraction of Mn²⁺ in the oxide as a function of the initial atom ratio Mo/Mn in the manganous nitrate solution.

Manganous ions in the oxide

The electron spin resonance (e.s.r.) method was used to study some of the oxides [5]. At 25 °C, two waves were found, one broad, corresponding to MnO₂ and one sharp, corresponding to manganous ions. At 77 K, which is below the Curie point for MnO₂, the broad wave disappeared as the oxide changed from a paramagnetic to an anti-ferromagnetic state. The sharp wave was still present, and could be measured without interferences from the wave due to MnO₂. In this way the amount of manganous ions present in the different oxides could be determined.

The results of the e.s.r. measurements are shown in Fig. 3. As can be seen, with the oxides decomposed at 135 °C the amount of manganous ion decreases as the molybdenum trioxide in the manganous nitrate solution is increased. Oxides decomposed at 180 °C show no such tendency. As only a few samples were tested, one cannot conclude that this dependence of manganous ion content on the temperature of decomposition has been definitely established.

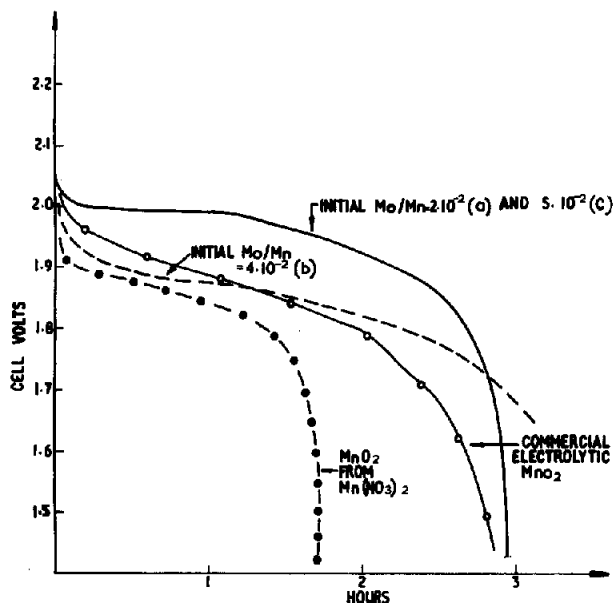


Fig. 4. Voltage-time curves for commercial electrolytic MnO_2 and MnO_2 containing various amounts of molybdenum. Decomposition temperature 135°C . Discharges at -20°C and 60 mA of the cell $\text{MnO}_2/8N \text{H}_2\text{SO}_4/\text{Zn}$. (a) Initial Mo/Mn ratio 2×10^{-2} , oxide Mo/Mn ratio 3.5×10^{-3} , x value 1.959; (b) initial Mo/Mn ratio 4×10^{-2} , oxide Mo/Mn ratio 5.5×10^{-3} , x value 1.952; (c) initial Mo/Mn ratio 5×10^{-2} , oxide Mo/Mn ratio 5.7×10^{-3} , x value 1.950.

X-ray diffraction analysis

X-ray diffraction analysis shows that the oxide has a tetragonal structure corresponding to pyrolusite. No change in the structure was observed when molybdenum was added [6].

Molybdenum free MnO_2 shows strong fluorescence when a CuK_α^{12} filter is used. The fluorescence decreased with increasing molybdenum content, and may be related to the manganese ions present.

Electrode behaviour

Electrode preparation

The electrodes were prepared in the same way as described earlier [1]. 1.5 g of a 85 : 15 oxide-graphite mix were pasted with 0.7 ml binder solution (5 g carboxymethylcellulose*, TB-253, dissolved in 300 ml distilled water).

The paste was applied to both sides of a 0.05 mm thick lead foil held in a 255 mm \times 255 mm Lucite frame. In accordance with the procedure in [1] the lead foil was perforated with a series of small holes to promote

*Chemical Developments of Canada Ltd.

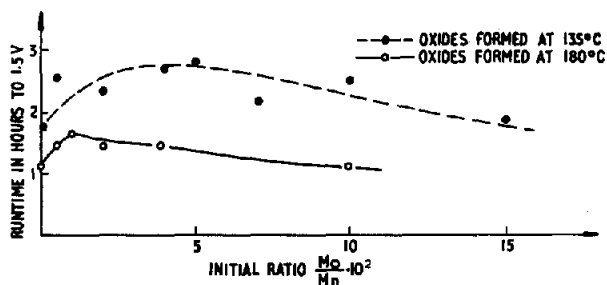


Fig. 5. Run time of $MnO_2/8N H_2SO_4/Zn$ cells as a function of the initial atom ratio Mo/Mn in the manganous nitrate solution. Discharges at $-20^\circ C$ and 60 mA.

adhesion of material, and oxidized for 2.5 min before the paste was applied. After drying for an hour before a fan, the pasted electrode was compressed at 48 MP and dried overnight. For fuller details, ref. [1] should be consulted.

Discharge of the electrodes

The electrodes were discharged at $-20^\circ C$ between two zinc sheets in 8 N H_2SO_4 . The discharge current was 60 mA (4.65 mA/cm^2 referred to the geometric area).

The electrodes were allowed to stabilize on open circuit before they were discharged. The end point of discharge was taken as 1.5 V.

Figure 4 shows some of the best results obtained with different types of oxide. As seen, far better results are obtained using oxides containing molybdenum than using oxides without. The molybdenum containing oxides are even better than the electrolytically formed manganese dioxide. Based on Fig. 4, it was found that: (1) up to 90% more energy (Wh) was obtained when molybdenum-doped manganese dioxide was used instead of manganese dioxide made in the same way, but without molybdenum; (2) compared with plates made up from battery-grade electrolytic manganese dioxide 10% more energy was obtained; (3) a higher voltage during the discharge could be obtained when molybdenum-doped manganese dioxide was used instead of electrolytic manganese dioxide.

In Fig. 5 the time before 1.5 V is reached is plotted as a function of the amount of molybdenum trioxide in the manganous nitrate solution. The points correspond to the average of several experiments.

It is seen that maximum values are obtained for oxides decomposed at both 135° and $180^\circ C$. The value is, however, much lower for oxides decomposed at $180^\circ C$ than for oxides decomposed at $135^\circ C$.

Discussion

The results show that the presence of molybdenum has a marked effect on the chemical composition as well as on the electrochemical behaviour of

manganese dioxide. The decrease in available oxygen with molybdenum increase is too great to be explained merely by a binding of oxygen to the molybdenum (as MoO_3). There is in addition a decrease in manganous ion content which is found at 135°C and which tends to increase the amount of available oxygen. It seems therefore likely that the molybdenum either creates oxygen vacancies or promotes manganese ions into interstitial positions.

The decomposition temperature seems to be of major importance. Although a maximum in the electrode performance is found for both decomposition temperatures (135° and 180°C), the greatest effect of molybdenum is found at the lower temperature. Good electrical performance is obtained where the available oxygen is highest and manganous ion concentration is the lowest. The results indicate that both were achieved to a greater extent at 135°C than at 180°C . If still lower temperatures could be used, oxides with even better electrode performance might be obtained.

The best electrodes in this work were prepared from oxides decomposed at 135°C when just sufficient molybdenum had been added to bring both the available oxygen and the manganous ion concentration to their minimum values (compare Figs. 2, 3 and 5). The exact connection between the molybdenum content and oxide composition on the one side and the electrochemical behaviour on the other side is not yet entirely clear from the existing results. In addition to the parameters already examined, other parameters, such as decomposition temperature and time might also prove to be important. The present report must therefore be treated only as a presentation of preliminary results. Further experiments should be done.

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