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An Oxygen Concentration Profile of a MnO_2 Particle after Discharge Service

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The behavior of oxygen in a manganese dioxide depolarizer discharged in a Leclanche-type test cell down to a cut-off voltage of 0.7 V was visually examined by means of electron probe microanalysis. The oxygen concentration profile of a typical MnO_2 particle of about 50 μ in diameter showed that the relative amount of oxygen at the surface and along the pores inside was evidently reduced due to the discharge reaction invading 5 to 10 μ towards the inner part of the particle, indicating that the discharge primarily took place in these portions and involves a process of releasing oxygen from sites at the outermost surface and along the pores. The region which contains these lower oxide portions was observed to be 20—30% of the total cross-sectional area, implying that the utility factor of MnO_2 as a depolarizer was accordingly of the order of 20—30%. It was suggested that enhancement of the use of pores or cleavages during a discharge would generally be beneficial to the service life as a depolarizer, better than merely reducing the particle size of the material.

The present paper provides results of an electron probe microanalysis of an MnO_2 specimen which was under discharging service as a depolarizer in a Leclanche-type wet cell. The purpose here is to visually examine relative concentrations of oxygen at the surface and the inner part of the MnO_2 particles during the discharge reaction.

Many years ago[1] the "polarization" of MnO_2 in a cell was explained by the formation of discharge products on the surface. In 1931, Keller[2] advanced the view that electric discharge of MnO_2 resulted in the formation of a solid solution of MnO_2 with a lower oxide of manganese and this material would degrade the electromotive force of the original MnO_2. Since then, many basic investigations have been carried out concerning the discharge mechanism of MnO_2 in terms of the primary discharge products of the MnO_2 electrode.[3] Changes in the X-ray diffraction pattern of MnO_2 during discharge were examined, as a means of revealing the reduction stages of the depolarizer in a cell, by various investigators including Matsuno,[4] McMurdie[5] and Copeland and Griffith.[6] These reports describe the formation of lower oxides and hydroxides of manganese as possible products in the discharge of MnO_2.

In recent years, a newly developed technique of electron probe microanalysis has been increasingly used in such fields as metallurgy and earth sciences in determining the nature of very small volumes of polished thin sections of alloys or mineral mounts. The principle is that the X-rays generated by the impact of the electron beam are characteristic of the elements present, and their intensity is an approximately linear function of concentration.[7]

1) E. Divers, *Chem. News*, **46**, 259 (1882).
2) A. Keller, *Z. Elektrochem.*, **37**, 342 (1931).
3) *E. g.*, W. C. Vosburgh, *J. Electrochem. Soc.*, **106**, 839 (1959); A. B. Scott, *ibid.*, **107**, 941 (1960); H. Bode, A. Schmier and D. Berndt, *Z. Elektrochem.*, **66**, 586 (1962); K. Sasaki, "Denchi Handbook," Denki-Shoin, Tokyo (1964), p. 265.
4) S. Matsuno, *Denki Kagaku*, **12**, 2 (1944).
5) H. F. McMurdie, *Trans. Electrochem. Soc.*, **86**, 313 (1944).
6) L. C. Copeland and F. S. Griffith, *ibid.*, **89**, 495 (1946).
7) J. Zussman, "Physical Methods in Determinative Mineralogy," Academic Press, London and New York (1967), p. 215.

If the MnO_2 during discharge produces a lower oxide or oxides of manganese by releasing the oxygen from MnO_2, a change in the relative concentration of oxygen at the reduced portions of the material may no doubt be visually observable, at least qualitatively, by differentiating the characteristic OK_α rays coming from the cross-sectional area of a thin section of MnO_2.

The present work has been performed in an attempt to observe the coexisting phases of reduced oxygen concentrations more directly by means of the electron probe microanalytical technique, to visualize how and where the reduction of the individual MnO_2 particles will proceed as the discharge takes place.

Experimental

Material. Electrolytically synthesized manganese dioxide was commercially available with an approximately 200 mesh fineness. This material was of a typical γ-type MnO_2 containing more than 91—93% MnO_2, and is currently used as a standard source of battery-grade manganese dioxide.

Procedures. (a) Discharging cell: A 5 g quantity of MnO_2 material was incorporated into a Leclanche-type test cell. The test cell was constructed by a method similar to that described in "Japanese Industrial Standards",[8] where 20 m*l* of a mixed solution of $NH_4Cl + ZnCl_2$ with a pH of 5.4 is provided as an electrolyte. A discharge with this type of wet cell was conveniently employed for the present purpose because of the ease of separating the MnO_2 after discharge from the cathode mix of the MnO_2 and acetylene black, rather than the paste-type cathode mix of a commercial dry battery. The cell construction used is shown in Fig. 1. A continuous discharge was performed on a fixed resistance of 10 Ω from an initial voltage of 1.6 V down to a cut-off voltage of 0.7 V.

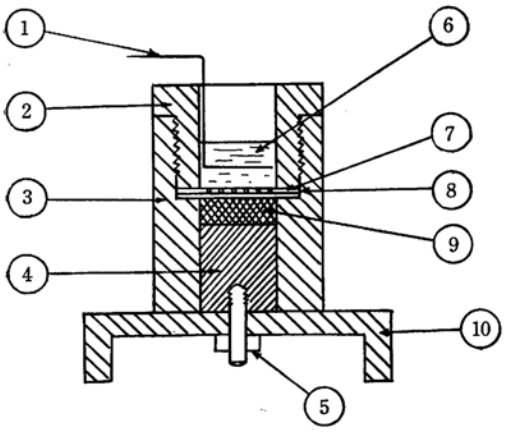

Fig. 1. Construction of the discharge cell used. (1): Zinc anode, (2): Anode bobbin, (3): Cathode bobbin, (4): Carbon rod, (5): Cathode terminal, (6): $NH_4Cl+ZnCl_2$ electrolyte, (7): perforated plate, (8): filter paper, (9): MnO_2 + acetylene black, (10): Bottom plate. (JIS K-1467 (1965))

8) JIS K-1467 (1965).

(b) Electron probe microanalysis: The cathode mix after discharge was washed and air dried. The dried sample was mixed with a polyester resin and set into a shape having a well-polished surface, and was put in an electron probe microanalyzer. This instrument was operated under the following set of conditions: accelerating voltage, 10 kV; average electron beam intensity, 0.04 μA; characteristic X-ray, OK_α; and magnification, 750. A concentration profile of the characteristic OK_α rays, integrated as well as discriminated, was taken by scanning the cross-sectional area of the MnO_2 in parallel with recording the absorbed electron image, focussing on a typical particle about 50 μ in diameter.

Results and Discussion

Figs. 2(a), 2(b) and 2(c) are a series of electron probe microanalyses for the cross-sectional area of a typical MnO_2 particle discharged down to a cut-off voltage of about 0.7 V, where Fig. 2(a) is the absorbed electron image of the profile with a magnification of 750. Figure 2(b) is a discriminated scanning of OK_α with the same magnification, which appears as an ensemble of small light spots across the same cross-sectional area as in Fig. 2(a). It is interesting to note that some darker portions cover the surface of the discharging particle and occurs along cleavages, or pores, near the surfaces of the body in Fig. 2(a), and in a corresponding manner in Fig. 2(b), the discriminated OK_α spots from the oxygen are less distributed at the border area between the cross-section and the background and around the pores in that area, reflecting a reduction in oxygen concentration in these portions. Especially the pores, either closed or open, of Fig. 2(a), are clearly observable as black voids in the upper-left areas lacking in white spots from oxygen in Fig. 2(b).

Fig. 2(c) is a photograph of the integrated intensities of the OK_α rays coming from oxygen

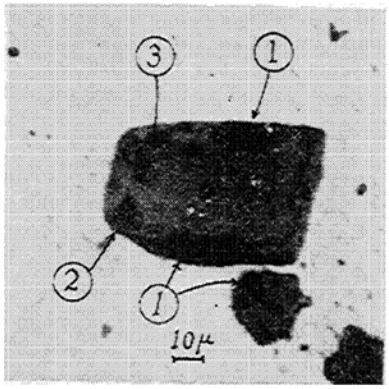

Fig. 2(a). Absorbed electron image of a profile of MnO_2 particle after discharge service. (1): discharged surfaces, (2): discharged open pore, and (3): discharged closed pore near the surface.

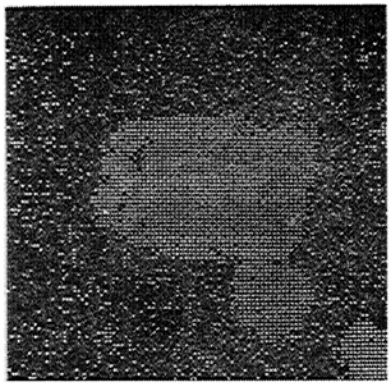

Fig. 2(b). Discriminated characteristc OK_α image scanned across the same profile of Fig. 2(a), showing that the corresponding discharged portions are less distributed with white spots which reflect the relative intensities of the characteristic OK_α rays coming from the oxygen of the cross sectional area. (Background: polyester resin of mounting piece)

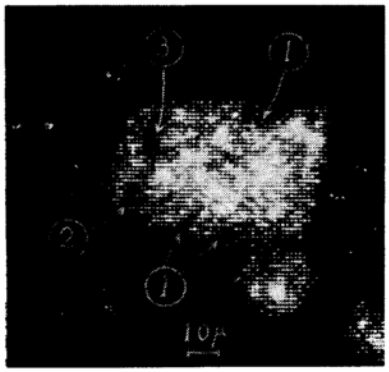

Fig. 2(c). Integrated characteristic OK_α image scanned across the same profile of Fig. 2(a), representing a well-defined light and shade of relative concentrations of oxygen of the profile. (1): discharged surfaces, (2): discharged open pore, and (3): discharged closed pore near the surface.

atoms of the same particle showing a more well-defined light and shade in the concentration profile. From a comparison of Fig. 2(c) with Fig. 2(b), it is clearly seen that the outermost surface of the particle and the vicinity around the pores are observed to contain a lesser amount of oxygen due to the reduction of MnO_2 in those portions, while the inner part of the particle is brighter, showing that the bulk still contains oxygen in the unused MnO_2.

It is noted that the parallel use of Figs. 2(a), 2(b) and 2(c) have provided a visual observation, in a sense, of the result that the discharge took place primarily at the surface and the pores, as previous workers pointed out the importance of the surface characteristics of MnO_2 including the surface area[9,10] and the pore distribution.[11,12] Furthermore, the present example with a 50 μ-particle suggests that the extension of the pores or cleavages in the MnO_2 body is seen to be roughly of the order of 10 μ. The initial pore openings have not been detected here, because the magnitude of a pore diameter is too small, previously calculated to be less than 400 Å by Cahoon[12] and predominantly 180 Å by Kozawa.[11] However, the results of Figs. 2(a), 2(b) and 2(c) show that the region containing a lower oxide of manganese, which was initiated along the micropores as well as at the surface, has invaded about 5 to 10 μ toward the inner part of the MnO_2 particle before decaying to the cut-off voltage of 0.7 V, and these invaded regions became detectable by the microanalytical method.

It also follows from an examination of the pictures that if the utility factor of the MnO_2 particle as depolarizer may be represented as a ratio of the total cross-sectional area of the particle to the darker area of reduced oxygen concentration emerging in the profile, the percentage will be 20—30% in this particular case of discharge down to a cut-off voltage of 0.7 V, which potential is well below that of the terminating voltage employed in most cases[13] when specifying the service life of a cell. This is an important observation as it shows the possibility of revealing changes in the solid phase during discharge in a cell system, provding useful data for industrial applications as well as for basic investigations of MnO_2 depolarizer, suggesting for instance that a treatment of the material to enhance a better use of the functions of cleavages or pores will be more beneficial to the service life as depolarizer than merely reducing the particle size alone.

Summary

Visual observation has been carried out with an oxygen concentration profile of an MnO_2 particle after discharge service down to 0.7 V in a Leclanche-type wet cell, by surveying the relative intensities of OK_α rays by means of an electron probe microanalytical technique. The roles of the pores inside the particle as well as the surface on the discharge process has been established by visually observing that the relative oxygen concentration of these portions becomes less after discharge. A covering of the MnO_2 by these lower oxide portions

9) M. Fukuda, T. Hirai and H. Manabe, *Denki Kagaku*, **27**, 204 (1959).
10) A. Kozawa and R. A. Powers, *Electrochem. Tech.*, **5**, No. 11—12, 535 (1967).
11) A. Kozawa, *J. Electrochem. Soc.*, **106**, 552 (1959).
12) N. C. Cahoon and M. P. Korver, *ibid.*, **109**, 1 (1962).
13) *E. g.*, G. W. Vinal, "Primary Batteries," John Wiley & Sons, Inc., New York (1961), p. 111; JIS C-8501 (1963); W. J. Hamer, *Electrochem. Tech.*, **5**, No. 11—12, 493 (1967).

is observed in a ratio of 20—30% of the total cross-sectional area. It is indicated that the discharge reaction of an MnO_2 particle involves a process of releasing oxygen from the sites of the outermost surface and along the pores.

The possibility is suggested for the use of the microanalytical examination as a powerful tool in interpreting how and where the discharge reaction proceeds across the cross-sectional area of the MnO_2 particle and in pursuing better performance for the material as a depolarizer in a cell.

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