

THE MOLYBDENUM TRIOXIDE DOPED MANGANESE DIOXIDE ELECTRODE: 2. ELECTRON SPIN RESONANCE STUDIES OF DOPED MANGANESE DIOXIDES

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Summary

Electron spin resonance spectroscopy (e.s.r.) has been used to study a series of molybdenum oxide doped manganese dioxides. The e.s.r. results show that both the surface area of the manganese dioxide as well as the Mn^{2+} concentration in the material depends on the amount of molybdenum oxide added. Determination of these quantities is of interest since the work of Våland indicates that they are related to the electrochemical characteristics of the manganese dioxides.

Résumé

La spectroscopie de resonance paramagnétique électronique a été utilisée afin d'étudier une série de bioxydes de manganèse additionnés d'oxyde de molybdène. Les résultats ont révélé que l'étendue de la surface, ainsi que la concentration du Mn^{2+} dans le bioxyde de manganèse, dépend de la quantité d'oxyde de molybdène qui a été ajoutée. La détermination de ces quantités est d'un grand intérêt, car le travail de Våland indique qu'elles sont liées aux caractéristiques électrochimiques des bioxydes de manganèse.

Introduction

The structure and solid state properties of manganese dioxides are of considerable interest because of the use of this oxide as a depolarizer in a variety of battery systems. Some of the properties of manganese dioxides that have been studied previously include crystal structure, electrical conductivity, magnetic susceptibility, particle size and shape, surface area, porosity, thermal properties and infra-red spectra.

This work was undertaken as a result of the work by T. Våland, reported in Part 1, which showed that the electrochemical performance of manganese dioxide can be substantially improved by doping with molybdenum trioxide. In the present work, the electron spin resonance (e.s.r.) spectra of a series of molybdenum trioxide doped manganese dioxides was measured in an attempt to correlate the physical and chemical characteristics of the oxide, that can be determined using this technique, with the electrochemical characteristics of the manganese dioxide.

Experimental

All of the doped manganese dioxides used in this work were prepared by T. Våland. The method of preparation and electrochemical properties of these oxides have been described in detail in Part 1. The method of preparation involved decomposition of manganous nitrate solutions containing differing amounts of molybdenum trioxide by heating in an oven at either 135 °C or 180 °C. (Referred to later as the 135° and 180 °C series of oxides.)

E.s.r. measurements were made using a Varian V-4500 ESR spectrometer. To make measurements at other than room temperature or 77 K, a Varian variable temperature cavity insert was used. A liquid nitrogen dewar insert was used to make measurements at 77 K.

In order to make quantitative concentration measurements, a dual e.s.r. cavity was used with a reference MnSO_4 sample in one cavity and the sample to be measured in the other. In order to compare the concentration in the measured sample with the reference sample which had in general a different linewidth, the relation $I(\text{ref})/I(\text{sample}) = (W^2 \times h)_{\text{ref}}/(W^2 \times h)_{\text{sample}}$ was used. W is the linewidth and h the peak height of the e.s.r. line. This relationship is valid for both Gaussian and Lorenzian lines. In using the above relationship to obtain relative intensities it is assumed that the shape of the lines is the same (*i.e.* either Gaussian or Lorenzian).

Results and discussion

General description of the e.s.r. spectrum of the doped manganese dioxides

The electron spin resonance spectrum of the manganese dioxides consists (Fig. 1) in general, of an overlap of an intense broad line (linewidth ≈ 2500 gauss) at $g = 2.1$ due to MnO_2 and a much narrower line (linewidth ≈ 200 gauss), of variable intensity depending on the sample, due to a Mn^{2+} impurity in the samples at $g = 2.0$. Neither line shows evidence of hyperfine or spin-spin interactions presumably because the lines are exchange narrowed by interaction with paramagnetic neighbours. MnO_2 is known [1] to be antiferromagnetic with a Curie point of -189 °C. In common [2] with other antiferromagnetic materials, a marked broadening and a decrease



Fig. 1. Typical e.s.r. spectrum of a molybdenum trioxide doped manganese dioxide.

in peak height of the e.s.r. line is observed as the temperature is lowered in the region of the Curie point. The width of the Mn^{+2} line on the other hand was found to be essentially independent of temperature. This indicates that this signal is not due to massive MnO (*i.e.* MnO "islands") since it is also antiferromagnetic and shows [2] a broadening with temperature similar to MnO_2 . The Mn^{+2} signal is assumed to be due to the replacement of Mn^{+4} ions by Mn^{+2} ions in the MnO_2 lattice.

Measurement of the changes in MnO_2 linewidth and peak height with temperature

The changes in linewidth and peak height of the e.s.r. spectrum due to MnO_2 as a function of temperature are shown in Figs. 2 and 3 for a doped manganese dioxide sample. The change in total absorption, as determined [3] by the expression, intensity \propto (linewidth)² \times (peak height), is shown in Fig. 4. These results indicate a decrease in susceptibility with temperature which is consistent with manganese dioxide undergoing a paramagnetic-antiferromagnetic transition in the temperature region investigated. This finding is not in agreement, however, with the work of

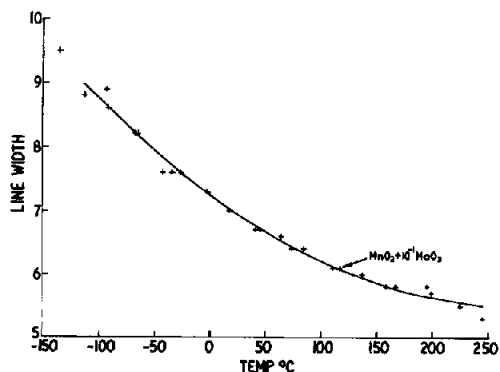


Fig. 2. Variation of e.s.r. linewidth as a function of temperature.

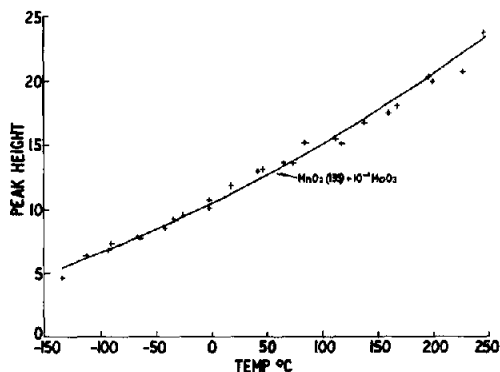


Fig. 3. Variation of e.s.r. peak height as a function of temperature.

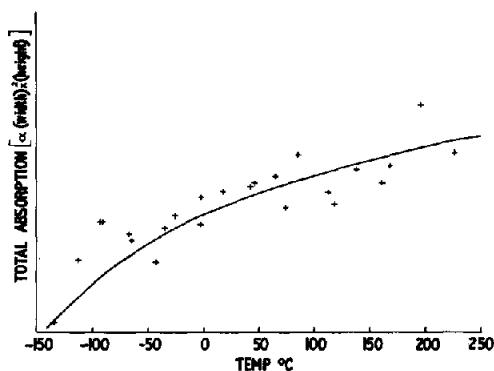


Fig. 4. Variation of e.s.r. absorption as a function of temperature.

Selwood *et al.* [4] which showed that most manganese dioxides of battery interest were magnetically dilute and showed an increase in susceptibility with temperature indicating paramagnetic behaviour over a similar temperature range. The reason for this discrepancy is not understood.

Measurement of the effect of doping on MnO₂ linewidth

It was noticed that the various doped and undoped manganese dioxides had significantly different linewidths for the MnO₂ peak. As has been mentioned previously, the e.s.r. signal due to MnO₂ consists of a single, very broad line with no evidence of hyperfine or spin-spin interactions. In concentrated samples such as these the e.s.r. lines are exchange narrowed [5, 6] because of interactions with its paramagnetic neighbours (*i.e.* the MnO₂ spectrum would be much broader and more complex in the absence of these interactions). The width of the line is thus determined by the number and location of the paramagnetic neighbours. Since the X-ray diffraction results [6] indicate that there is no change in lattice spacing, it is reasonable to assume that the changes in e.s.r. linewidth from sample to sample are associated with changes in the average number of paramagnetic neighbours

TABLE 1
Room temperature MnO₂ linewidths

Doping	Linewidth (G)
135 °C oxides	
0	2400
1×10^{-2}	2600
2×10^{-2}	2800
7×10^{-2}	2800
10^{-1}	3200
180 °C oxides	
0	2850
2×10^{-2}	2600
4×10^{-2}	2550
10^{-1}	2500
Other oxides	
Electro ore	2600
KMnO ₄ + H ₂ O ₂	1700
Gabono	~1500

(Z) possessed by each Mn⁴⁺ ion. Thus as the structure of the oxide becomes more disperse, that is has a higher surface area, the linewidth will increase because of reduced exchange narrowing effects. The phenomenon of exchange narrowing has been treated quantitatively by VanVleck [5] and Anderson and Weiss [6]. Their results indicate that the quantitative relationship between linewidth and the number of paramagnetic neighbours is complex. In the approximation that major magnetic interactions (dipolar and spin-spin) contributing to the linewidth are intramolecular rather than intermolecular and that the lattice spacing (and hence the exchange constant J) is independent of doping and isotropic, then the linewidth will be inversely dependent on Z , the number of paramagnetic neighbours. This is the relationship that we will assume to hold in the present work.

From the above discussion it is seen that the width of the line is determined by the number of paramagnetic neighbours and, in this way, the width can be used as a measure of the diffusivity or surface area of the manganese dioxide sample (*i.e.* the more diffuse the structure of the oxide the fewer paramagnetic neighbours each Mn⁴⁺ ion will possess). Similar arguments have been used by Selwood *et al.* [4] to explain the lowering of the Curie point in dispersed chromium oxide.

Room temperature linewidth results for the two series of doped manganese dioxide are given in Table 1. It will be noted that for the 135 °C series of oxides, there is a regular increase in e.s.r. linewidth with MoO₃ doping indicating that the structure of these manganese dioxides is becoming more diffuse as the doping increases. This interpretation is supported by the observation that there is a marked decrease in density of the oxides at high dopings.

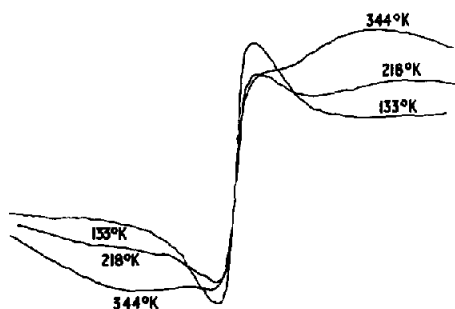


Fig. 5. Influence of temperature on the e.s.r. spectrum of a doped manganese dioxide.

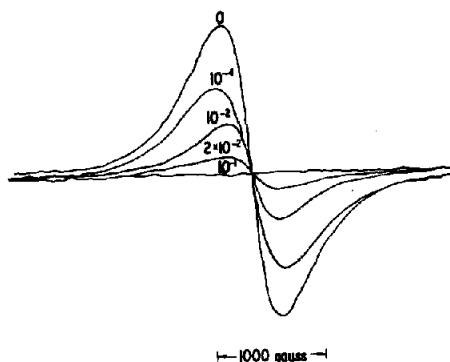


Fig. 6. Effect of doping on the intensity of the e.s.r. line due to Mn^{2+} .

TABLE 2

Concentration of Mn^{+2} in doped manganese dioxides

Doping	Concentration $\frac{Mn^{+2}}{Mn}$
135 °C oxides	
0	8×10^{-3}
10^{-4}	6.3×10^{-3}
1×10^{-2}	1.8×10^{-3}
2×10^{-2}	8×10^{-4}
10^{-1}	0
180 °C oxides	
0	1.3×10^{-3}
2×10^{-2}	2×10^{-3}
4×10^{-2}	4×10^{-3}
10^{-1}	2×10^{-3}

The linewidths of the manganese dioxides formed at 180 °C on the other hand were found to decrease slightly with increasing doping indicating a slight reduction in surface area. Table 1 also includes linewidth data for other manganese dioxides for comparison.

Measurement of the Mn^{2+} concentration in and determination of the stoichiometry of manganese dioxides

As has been mentioned previously the e.s.r. spectrum of the doped manganese dioxides consists of an overlap of two lines—a broad MnO_2 peak and a much narrower peak due to Mn^{2+} impurities. In addition the linewidth of the MnO_2 peak increases rapidly with decreasing temperature whereas the Mn^{2+} linewidth is temperature independent. The broadening of

the MnO_2 peak with decreasing temperature is so great in fact, that at 77 K one only sees the Mn^{2+} signal. By recording spectra at 77 K then, one can obtain an estimate of the concentration of Mn^{2+} in the manganese dioxide even in cases where the Mn^{2+} signal is obscured by the more intense MnO_2 signal at room temperature. Figure 5 shows the e.s.r. spectrum of a doped manganese dioxide at various temperatures to illustrate this transition. By making measurements at 77 K we have determined the Mn^{2+} concentration in the various doped manganese dioxides. These results are given in Table 2 and illustrated in Fig. 6 for the 135 °C manganese dioxides. Våland has already noted (in Part 1), that there appears to be a correlation between the Mn^{2+} concentration and the electrochemical performance of the oxides. It is also interesting to note that the Mn^{2+} concentration in the oxide decreases as the diffusivity or surface area of the manganese dioxide increases. It is possible that decrease in the Mn^{2+} impurities with increasing surface area may be related to the relative ease in washing these impurities from the manganese dioxide after preparation.

If it is assumed that the manganese dioxide (MnO_x where $x < 2.0$) is a mixture of the manganese oxides MnO_2 , Mn_2O_3 and MnO then the determination of the Mn^{2+} concentration provides a method of determining the stoichiometry of the oxide when combined with an available oxygen determination.

For example in the 135 °C undoped manganese dioxide, it has been found from an available oxygen determination (Part 1) that the formula may be written $\text{MnO}_{1.985}$. The fraction of MnO in the same sample has been determined from the e.s.r. measurement to be 0.008.

In general we can write:

$$\text{MnO}_x = a\text{MnO}_2 + b\text{Mn}_2\text{O}_3 + c\text{MnO} \quad (1)$$

where $x = 2a + 3b + c$ and

$$1 = a + b + c \quad (2)$$

Substituting the values of $x = 1.985$ and $c = 0.008$ from the example above into eqns. (1) and (2) gives $a = 0.978$, $b = 0.007$ and $c = 0.008$.

Conclusions

This work has indicated that e.s.r. methods can provide a substantial amount of information about the structure of manganese dioxides. Using e.s.r. spectroscopy, it has been found possible to measure directly the concentration of Mn^{2+} in the oxides. This result, when combined with an available oxygen determination, provides a method for determining the relative amounts of MnO_2 , Mn_2O_3 and MnO in the sample. It has also been found that there is a variation in linewidth of the MnO_2 signal from sample to sample. This effect has been attributed to changes in the surface area of the oxides and should provide a useful method for measuring changes in surface area.

From these results, it appears that the e.s.r. method should be useful in helping to characterize the manganese dioxides that are used for battery purposes and also in the study of the reactions that occur at a manganese dioxide electrode during charge and discharge.

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