

## Short Communication

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# Electrolytic manganese dioxides for battery applications: studies using electron paramagnetic resonance

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### Abstract

Electron paramagnetic resonance (EPR) data are presented for four different samples of electrolytic manganese dioxide (EMD) that are intended for use in battery applications. The effects of graphite addition and discharge of active material are examined. Amongst the samples, wide differences in both the intercrystalline parameters and the number of available electrons in the conduction band are observed. The  $g$  factor is found to exhibit sensitive variations from sample to sample. In some samples, several types of manganese electrons can be detected. The extent of the  $\gamma$  phase – an essential aspect for aqueous electrochemical activity – can be assessed in samples.  $\text{MnO}_2$ -graphite agglomerates and reduction products of  $\text{MnO}_2$  are identified. The magnetism of active materials is explained from analysis of the EPR spectra.

### Introduction

Manganese dioxide is used in several types of cells, viz., aqueous (neutral and alkaline) [1, 2] and nonaqueous (lithium type) [3] systems. Electrons and holes participate in the conduction mechanism of this semiconductor [4]. Despite several publications, a true understanding of the structural aspects of manganese dioxide has yet to be reached. This is because  $\text{MnO}_2$  is a very complex material and exists in several varieties, e.g., natural manganese dioxide (NMD), chemically precipitated manganese dioxide (CMD), electrolytic manganese dioxide (EMD), etc. EMD has special properties that render it an essential material for batteries.

Even with EMD, the structural properties vary from source to source and are strongly dependent upon the conditions of production. Several anomalies exist in connection with the structure of EMD. Some researchers have claimed that EMD has the Nsutite, or the  $\gamma$ - $\text{MnO}_2$  structure, or a random intergrowth of pyrolusite and ramsdellite domains [5]. There is an alternative opinion that EMD does not belong to a diaspore matrix but rather to  $\epsilon$ - $\text{MnO}_2$  [6]. It is also argued that EMD consists of  $\beta$ - $\text{MnO}_2$  as a discrete phase [7]. Finally, it has been suggested that  $\gamma$ - $\text{MnO}_2$  exists in an infinite number of varieties in EMD [8].

Several techniques, including X-ray diffraction (XRD), have been used to study EMD. It has proved difficult to identify a particular polymorph solely on the basis

of routine XRD investigations, despite the fact that XRD is a powerful and widely-accepted tool. Therefore, it becomes necessary to compliment such studies with other techniques.

MnO<sub>2</sub> is paramagnetic by virtue of the presence of 3 unpaired electrons in the 3d orbitals of the Mn<sup>4+</sup> ion. In EMD, Mn<sup>3+</sup> occurs in a high-spin state with a (t<sub>2g</sub><sup>3</sup> e<sub>g</sub><sup>1</sup>) configuration. In addition, Mn<sup>3+</sup> has degenerate e<sub>g</sub> orbitals with one electron and is a Jahn–Teller ion. Thus, EMD is ideal for EPR studies. In EMD, the structure is usually interspersed with protons from the water of constitution; these are electron donors to the σ\* bond. (Note, the water content in EMD is an important feature.) EPR is capable of examining the interactions of protons with the MnO<sub>2</sub> lattice. Furthermore, the band structure of MnO<sub>2</sub> is still not fully understood. The EPR line shape can yield useful information on the conduction band. Grain size influences the physics of conduction in EMD [9]. Thus, intercrystalline parameters, as revealed by EPR line width, should provide useful information. It should be noted that good correlation has been already observed [10] between magnetic and electrochemical properties.

To the author's knowledge, the first EPR investigation of the structure of EMD, and its performance in batteries, is reported in this communication.

## Experimental

Four samples (I to IV) of battery-grade EMD from different manufacturing sources were examined. The first three samples were of Indian origin, while the remaining one was the international common sample IBA 18. For study in battery applications, the MnO<sub>2</sub> cathode was prepared with a EMD-graphite mix (20 wt.% graphite KS44) and carboxymethylcellulose–alkali gel binder. The MnO<sub>2</sub> sleeve cathode was compressed at a pressure of one ton. For a LR6 battery assembly, a 'kuralon' separator and a gelled zinc anode were used. The electrolyte was 40 wt.% KOH. One sample, II, was used for battery studies to explore the utility of EPR in investigating the MnO<sub>2</sub> electrode. The cell was discharged at 27 °C with a constant load of 5 Ω to a cutoff voltage of 0.75. The EPR spectra of the MnO<sub>2</sub> samples were collected at room temperature with a Varian E-112 EPR spectrometer. The frequency of the applied microwave field was ~9.5 GHz. To determine EPR *g* factors, DPPH (2,2-diphenyl-1-picrylhydrazyl) was used as a standard, since it has a sharp, singlet EPR spectrum with an accurately known *g* factor equal to 2.0037 ± 0.0002 [11].

## Results and discussion

The EPR data of the various samples of EMD are given in Table 1. The results of EPR analysis of MnO<sub>2</sub> electrode are shown in Table 2.

### *EPR of EMD samples*

The *H*<sub>0</sub> and *g* values of sample I suggest that the majority of manganese atoms occur in a Mn<sup>4+</sup> state and that the diffusion of protons in the crystal lattice is insufficient, i.e., indication of the absence of the γ-phase in significant amounts. The *g* values for Mn<sup>4+</sup> in the strong and moderate lines are higher than that characteristic for the ion. This indicates a positive polarization. In the second case, an ion with such great orbital *g* shifts is expected to relax quite rapidly. Weak EPR signals with

TABLE 1  
EPR parameters of EMD samples

Sample	Resonating field $H_0$ (Gauss)	Full line width at half maximum $\Delta H_{p-p}$ (Gauss)	Lande g factor	Asymmetry factor <sup>a</sup> A/B	Magnetic moment MM (emu/g)	Relative discharge performance in LR6 cells [12] <sup>b</sup> (%)
I	2900 (strong)	1450 (strong)	2.2796 (strong)	1.05	30.97	48
	1975 (moderate)	200 (moderate)	3.3478 (moderate) 1.9855, 1.9165 (weak)			
II	2938 (strong)	1275	2.2641 (strong)	0.90	30.50	52
	2563 (moderate)	75	2.5954 (moderate)			
III	3350 (strong)	2700	1.9767 (strong)	1.54	27.22	76
			2.3906, 2.3440, 2.2523, 2.2447, 2.1711, 2.1361, 2.0693 (weak)			
IV	3500	2500	1.8891 (strong)	2.25	27.83	100
			2.1260, 2.0825, 2.0344, 1.9885, 1.9221, 1.8625 (weak)			

<sup>a</sup>Ratio of low-field to up-field intensity.

<sup>b</sup>MnO<sub>2</sub> cathode prepared with 20 wt.% KS44 graphite and compacted at a pressure of 3 tons; discharge to a cutoff voltage of 0.75 V at 1  $\Omega$  load, IBA 18 taken as reference.

TABLE 2

EPR parameters of MnO<sub>2</sub> electrode

Sample	Resonating field $H_0$ (Gauss)	Full line width at half maximum $\Delta H_{p-p}$ (Gauss)	Lande $g$ factor	Asymmetry factor A/B
Fresh active material	2930	1180	2.2429	10.00
Discharged cathode material	3000	1140	2.1973	1.90

$g$  values of 1.9855 and 1.9165 indicate that substitution of Mn<sup>4+</sup> by Mn<sup>3+</sup> does take place, but only in small amounts. But for these substitutions, the material is highly stoichiometric. Further, the occurrence of an A/B value around 1.05 suggests that only a moderate number of electrons could be released by the sample on discharge. A somewhat fine particle size is observed given the narrowing of the EPR line. The low  $H_0$  and A/B values lead to the conclusion that sample I, if used for alkaline cell assembly, might not yield the desired capacity. Indeed, LR6 cells made with this material yielded only moderate performance [12] (see Table 1).

Sample II is similar in structure to sample I, except for the absence of Mn<sup>3+</sup> ions in detectable amounts. The smaller line width, asymmetric nature and A/B values indicate that the performance of sample II will be slightly lower than that of sample I. This was confirmed by experiments on LR6 cells [12]. The fine crystalline nature of the sample, an undesirable feature for alkaline cell applications, is demonstrated by the small values obtained for  $\Delta H_{p-p}$ .

Sample III has a high A/B value (viz., 1.54) and, thereby, has a high electron-delivering capacity. The strong EPR line at 3350 Gauss is due to interactions with protons. The EPR line is not a pure singlet but is smeared with about 7 weak EPR signals. Multiple valence states of manganese give rise to a greater degree of non-stoichiometry. Internal strains in crystals, due to hydrogen saturation, result in a broadening of the EPR line. An increased coarseness in particle size can be inferred from the large  $\Delta H_{p-p}$  values. The greater degree of H<sup>+</sup> transport and structural disorder suggests the occurrence of the  $\gamma$ -phase in appreciable amounts. It appears that some submodifications of the  $\gamma$ -phase also occur. Thus, the highly asymmetric line shape, broad line width, smaller  $g$  values, and multiple EPR signals indicate a good electrochemical activity for sample III in alkaline cells. Indeed, other studies [12] showed the material to exhibit good performance in LR6 cells.

Sample IV is composed of a large amount of  $\gamma$ -phase as is evident from the low  $g$  values. The latter suggest excessive Mn-H<sup>+</sup> couplings and substitutions with Mn<sup>3+</sup> ions. Six weak EPR signals appear and the corresponding  $g$  factors indicate multiple valence states of manganese that are coupled with protons. Due to the presence of water, there is a critical slowing of the spin fluctuations. This leads to a reduction of the exchange narrowing between manganese atoms – the factor that is responsible for the observed increase in EPR line width. The broadened nature of the spectrum together with the high A/B values, suggests that, compared with the three other materials, sample IV will provide the maximum number of electrons per unit volume. Coarseness in particle size – a desirable feature for alkaline cell applications – is shown by the high  $\Delta H_{p-p}$  value. The combined influence of crystallite size, partial replacement of Mn<sup>4+</sup> by Mn<sup>3+</sup>, non-stoichiometric nature and intergrowth lattice

disorder (as revealed by EPR parameters) render sample IV the most suitable for alkaline battery applications.

#### *EPR of manganese dioxide cathode*

The EPR data of a  $\text{MnO}_2$  cathode using sample II reveal interesting features. On graphite addition, the A/B factor increases by a factor of about 11 (Table 2). This indicates an improvement in the electrical conductivity of the  $\text{MnO}_2$  sleeve cathode. As expected, the  $g$  factor of the cathode mix remains almost the same as that of the EMD. The slight reduction in line width relates to a decrease in the particle size of  $\text{MnO}_2$ . This is due to the compression and probable formation of  $\text{MnO}_2$ -graphite agglomerates. On fully discharging the  $\text{MnO}_2$  electrode, the A/B factor falls to 1.9. This value shows that the electrode has delivered its full capacity and that not many electrons can be released further by the electrode so as to deliver a meaningful current. The reduction in the  $g$  factor suggests that  $\text{H}^+$  ions have entered the crystal matrix.

A significant decrease in the line width is expected on discharge of the cathode material in view of the transformation of  $\text{Mn}^{4+}$  to  $\text{Mn}^{3+}$  and lower valency species. In practice, the lattice expansion of the cathode offsets this effect and, consequently, there is only a slight reduction in the line width. In fact, on reduction of the  $\text{MnO}_2$  electrode, replacement of  $\text{Mn}^{4+}$  and  $\text{O}^{2-}$  by ions with larger radii (i.e.,  $\text{Mn}^{3+}$  and  $\text{OH}^-$ , respectively) occurs and this leads to lattice dilation [13–15].

#### *Explanation of magnetism with EPR data*

The magnetic moment/g (MM) of samples, as revealed from magnetization experiments [12], is given in Table 1. It can be clearly seen that a decrease in the  $H_0$  value is associated with an increase in MM. In particular, the fall in  $H_0$  values below 3300 Gauss causes a significant rise in MM. This is in line with expectations as the EPR signal of manganese, which occurs around 3300 Gauss, is due to interaction with protons. It is well known that hydrogenation of  $\text{MnO}_2$  lowers the MM and causes  $H_0$  to occur at higher fields in the EPR spectrum. Two classes of magnetic phases are detected, samples I and II constitute one class, and samples III and IV the other class. The slight deviation exhibited by sample IV can be attributed to a quasi-static electronic ordering that gives rise to strong ferromagnetic superexchange interactions between  $\text{Mn}^{3+}$  ions that are mediated by oxygen ions in the  $\gamma$ - $\text{MnO}_2$  and result in a slight increase in MM.

## Conclusions

Studies using the EPR technique have yielded useful information on the structure and electrochemical activity of EMD. These investigations can account for the observed magnetism of the samples. As a consequence, EPR promises to be a powerful tool for evaluating the mechanism taking place at the manganese dioxide cathode in batteries. Multiple EPR signals, low  $g$  values, broad line widths and a highly asymmetric nature are characteristic of EMD that is best suited for application in alkaline cells.

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