Electron paramagnetic resonance in pyrolusite and cryptomelane manganese dioxides

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Electron paramagnetic resonance spectroscopy has been applied to identify the singular structural features of pyrolusite (β) and cryptomelane (α) manganese dioxides. At 77 K, the derivative linewidth of pyrolusite is reduced to that of cryptomelane and the $M_S = -3/2$ spin states in cryptomelane are affected by the changes in crystal field. Isothermal heating of cryptomelane in air at 100 °C for two days affects the $M_S = -5/2$ and $M_S = -3/2$ levels. The results seem to confirm the partial collapse of the lattice due to release of molecular water on heating.

The use of manganese dioxide as a cathode material for different types of electrochemical power sources is well known.[1–4] Amongst the different polymorphs of this unique material, the α and β forms (Fig. 1 and 2) are notable in the sense that these two fall on the extreme edges of a wide spectrum of different non-stoichiometric structures. Also, the α form hollandite-type MnO_2 has recently been found to be useful in lithium rechargeable batteries[5] whereas β polymorphs readily find applications in non-aqueous batteries.[6] So far characterisation of these groups has been carried out using conventional techniques, like X-ray diffraction, magnetic susceptibility,[7] electrical conductivity and thermoanalytical measurements,[8] which cannot be used for elucidating the subtle structural features of the dioxides. But electron paramagnetic resonance (EPR) spectroscopy enables precise investigation of the chemical environments around the manganese spins and lends itself as an elegant technique to the evaluation of manganese dioxides.[9] To our knowledge no exhaustive report is available on electron paramagnetic resonance in different MnO_2 samples. Hence, a variety of manganese dioxides are being studied by EPR spectroscopy in our laboratory to obtain valuable information about the structural parameters useful for battery assembly.[9]

In this paper pyrolusite (β-MnO_2 with near rutile structure) and cryptomelane (K^+-containing α-MnO_2) have been characterised with EPR measurements both at room- and liquid-nitrogen temperatures. A comparative study of the various EPR parameters for these samples is made using these experimental results.

Experimental

Fine powders of pyrolusite and cryptomelane chosen for the study were supplied by Union Carbide India Ltd., Calcutta, India. The samples were verified for their polymorph group by X-ray diffraction and scanning electron microscopy (SEM) examinations.

For electron microscopy, the samples were moistened with doubly distilled water and compacted into pellets of diameter 8 mm. Samples were glued on a specimen holder and sputtered with gold. A JEOL JSM-CF 35 scanning electron microscope operating at 15 kV was used.

EPR spectra of the samples were recorded with a Varian E-112 spectrometer at 77 and 300 K. DPPH was used as the '*g*' marker since it has a sharp, single EPR spectrum with an accurately known *g* factor equal to 2.0037 ± 0.002.[10] EPR measurements were also made on the international common sample IBA-18 (International Battery Associations common sample 18) as a reference.

Results and Discussions

Electron microscopy

As the morphologies of α- and β-MnO_2 are different, SEM was used to confirm the polymorphs. Pure and fully crystalline β-MnO_2 occurs in globular particles of 50–100 μm diameter (Fig. 3). Platelets of width 3 μm and length 20 μm are found in these globules (Fig. 4). The crystallites are smaller in KMn_8O_{16} (Fig. 5), and cryptomelane is not as crystalline as pyrolusite (Fig. 6).

EPR experiments at 300 K

The EPR (first derivative) characteristics are shown in Fig. 7. In pyrolusite [Fig. 7(*a*)] only a very broad singlet ($\Delta H_{p-p} > 2000$ G) is obtained. Since this phase is highly stoichiometric with the presence of Mn^{4+}, the occurrence of only one EPR signal is justified.[11] The large linewidth is indicative of the powdered polycrystalline nature of the sample, as β-MnO_2 is known to possess a preferred crystal orientation and is found to occur in globular particles[8] as seen in the electron micrographs (Fig. 3 and 4). This is also in concurrence with the higher electrical conductivity of the sample.[12] The good electrochemical performance in aprotic electrolytes[6] is prob-

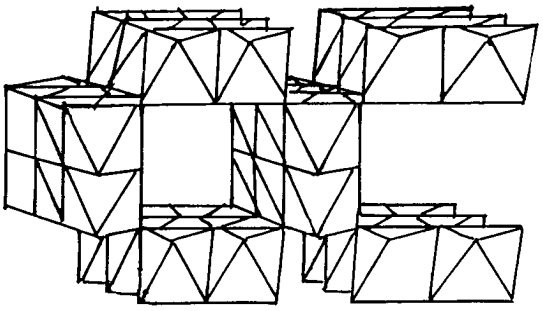

Fig. 1 Structure of α-MnO_2

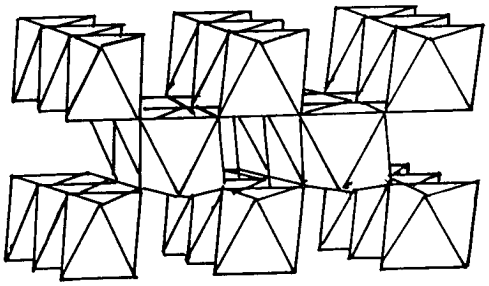

Fig. 2 Structure of β-MnO_2

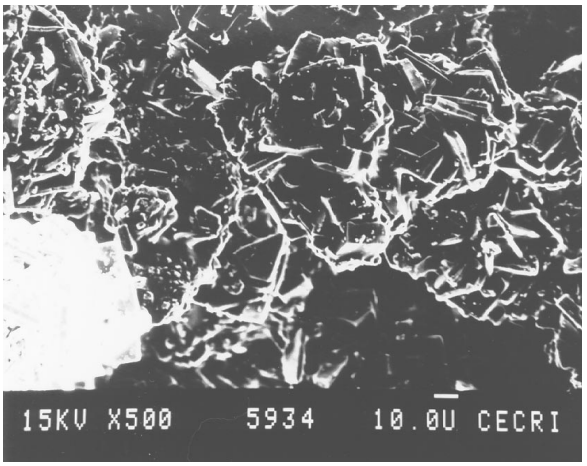

Fig. 3 Crystalline nature of β-MnO_2

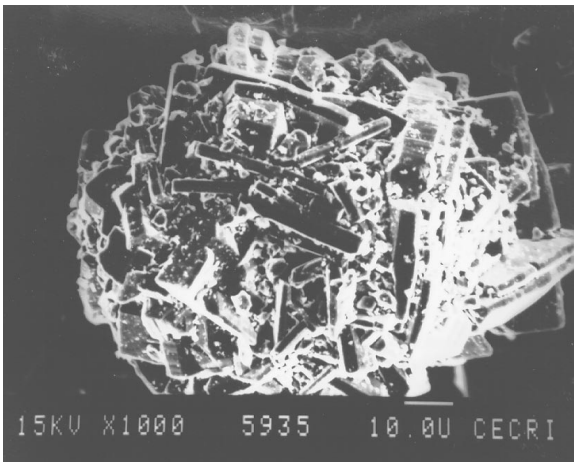

Fig. 4 Globular agglomerates of plates in β-MnO_2

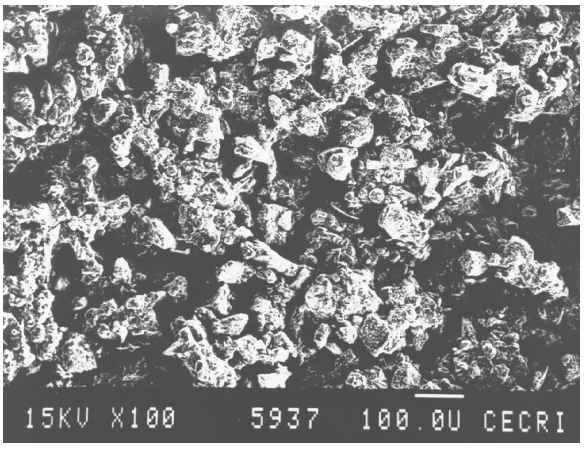

Fig. 5 Small crystallites in α-MnO_2

ably supported by the large ΔH_{p-p} values. This may be attributed to several factors, *e.g.* the degree of stoichiometry, the constituent water content and the particle size.

By contrast, five EPR lines are obtained for cryptomelane KMn_8O_{16} [Fig. 7(*b*)]. This is reminiscent of the six well resolved hyperfine structure components characteristic of Mn^{2+} which usually occur in its hydrated salts. These lines arise from the interaction of the ^{55}Mn nuclear spin with the electronic spins of Mn^{2+}: $-5/2$, $-3/2$, $-1/2$, $+1/2$, $+3/2$, $+5/2$ (nuclear magnetic spin quantum number, M_I). Only one set of hyperfine components appears in the observed spectrum.

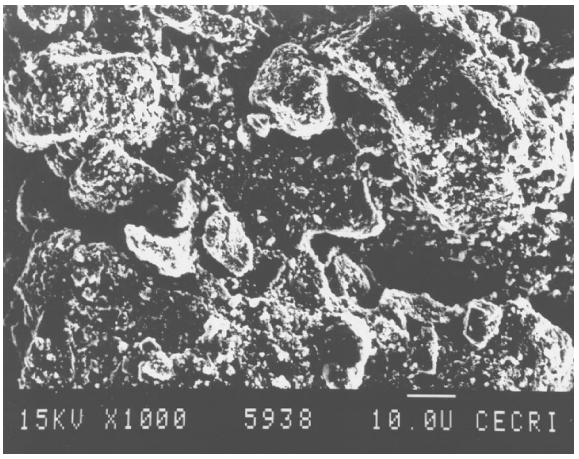

Fig. 6 Magnified view of particles in α-MnO_2

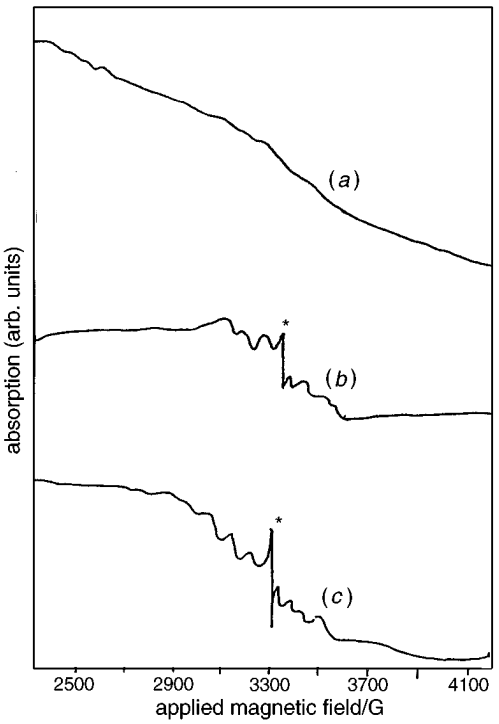

Fig. 7 EPR spectra of pyrolusite (*a*), cryptomelane (*b*) and heat-treated cryptomelane (*c*) at 300 K (*, DPPH)

However, the observed admixture of the absorption spectra due to $M_S = -1/2$ and $M_S = +1/2$ is indicative of spin–orbit coupling. This is in line with expectation since α-MnO_2 is non-stoichiometric and contains interactions with H^+ species (*i.e.* α-MnO_2 is actually $MnO_{2-\delta}$, the δ part is composed of H^+ ions in constituent water which interact with the manganese oxide lattice) and contains K^+ ions in its 2×2 tunnels.[13] Interestingly the first three lines occur at the same fields as in γ- and ε-MnO_2 samples (IBA 18) [Fig. 8(*a*)], which have very high electrochemical activity in alkaline media.[9] The remaining EPR signals occur at relatively high field as compared to IBA 18. This observed shift in *g* values for Mn positive spins may again be attributed to excess spin–orbit coupling in the α form as compared to the γ and ε samples. We find that the resonance occurs only over a narrow range as compared to the broad EPR spectra that usually occur in the γ and ε varieties. This could be one reason for the observed higher aqueous electrochemical activity of the ε and γ polymorphs over the pure α samples. The spectrum is extended in lower fields in IBA-18 as compared to pure α-MnO_2. Also there is a possibility that Mn^{2+} ions could be located on K^+ sites with a K^+ vacancy

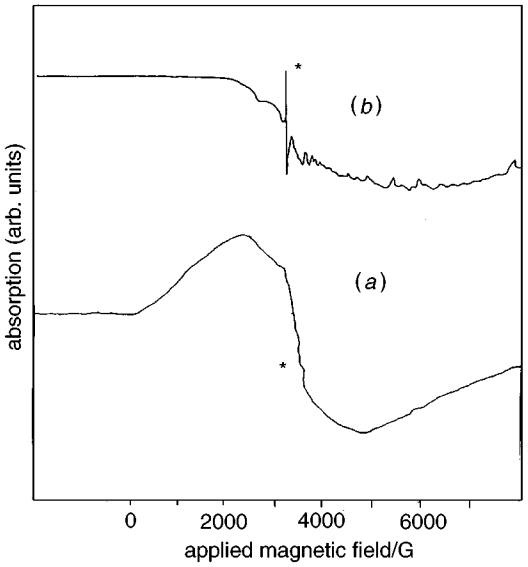

Fig. 8 EPR spectra of IBA-18 MnO_2 at (*a*) 300 K and (*b*) 77 K (*, DPPH)

nearby, and the hopping process could be connected with equivalent Mn^{2+} off-centre positions.[14] Additional complexities may arise due to the fact that in C_3 symmetry, the total of 252 degenerate levels of the d^5 configuration for the Mn^{2+} ion can be condensed into 126 doubly degenerate levels *i.e.* Kramer's doublets.[15]

In general, the spectra are mostly not well resolved, and although it appears that Mn^{2+} is present in some of them, this may only be a minority species. Thus some of the conclusions drawn may be rather speculative.

EPR experiments at 77 K

Interesting changes are revealed by low-temperature measurements in β-MnO_2 [Fig. 9(*a*)]. The linewidth is reduced to that of α-MnO_2. Thus, as the temperature increases, broadening of the paramagnetic resonance lines occurs due to spin–lattice interactions.

As MnO_2 is an n-type semiconductor, as revealed by our thermopower measurements,[16] it is worth studying EPR at low temperature as in the case of silicon.[17] The EPR lines from α-MnO_2 at 77 K [Fig. 9(*b*)] are almost the same as those at 300 K except that, as expected, they occur at lower fields. The derivative linewidth is also practically unchanged. This is unlike the γ and ε modifications which exhibit singular random variations between the 300 and 77 K spectra [Fig. 8(*b*)]. This is as expected as Mn^{2+} is a paramagnetic ion in an S state. Due to the fact that the functional orbital level is in an S state, the Mn^{2+} ion is only very slightly sensitive to changes in crystal field and broadening is not expected. Thus the spin–lattice interactions through electric field modulations (Kronig Van Vleck's mechanism) should not be effective in such ions. However, S-state ions can act only through admixtures of upper orbital states with non-zero orbital momenta. This explains the interactions made by the $-3/2$ levels at 77 K as revealed from the state of ions which appear to be located at non-cubic sites.

Influence of heat treatment

Heat treatment is carried out on some manganese dioxides to improve their electrochemical activity.[18] As such, studies in this direction are important. Three kinds of water have been observed in manganese dioxides:[8] (i) adsorbed (loosely bound) molecular water which is desorbed in the range 25–105 °C; (ii) interlayer molecular water bound more tightly and released

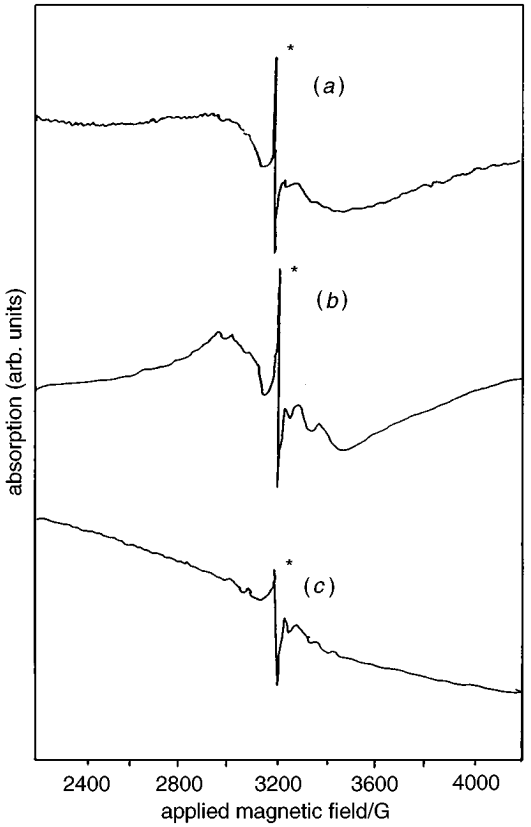

Fig. 9 EPR spectra of pyrolusite (*a*), cryptomelane (*b*) and heat-treated cryptomelane (*c*) at 77 K (*, DPPH)

up to 150–250 °C and (iii) condensing of OH groups or constituent water released in the range 105–500 °C.

β-MnO_2 has less than 0.1% adsorbed water[8] and is not expected to be very sensitive to heat treatments in the temperature range 25–105 °C. It will be interesting to study the structural changes occurring in α-MnO_2 on isothermal prolonged heating in air at around 100 °C as oxidation of Mn^{3+} ions to Mn^{4+} and changes in lattice structure due to the release of constituent water may occur, as has been observed by Ruetschi *et al.*[19]

The effect of heat treatment at 100 °C for 2 days on the structure was investigated for cryptomelane to study the changes occurring in the EPR lines. The 300 K spectra [Fig. 7(*c*)] indicate that although the α structure is maintained at this temperature, a tendency for EPR line broadening is observed.[4] The observed inhomogeneous broadening of Mn^{2+} may be due to random internal stresses depending on the thermal history of the sample or due to distribution of point defects. In the new spectrum, the $M_S = +3/2$ signal is well developed in contrast to the broadened nature before the heat treatment. Also, the upper symmetry of central peak is more resolved in the new spectrum whereas it was as high as the $M_S = -3/2$ peak before the heat treatment. Thus it is seen that, owing to isothermal heating in air at 100 °C, the manganese negative spin states are affected because of changes in local environment and oxidation state.

The new 77 K spectrum [Fig. 9(*c*)] reveal interesting features. The broadened nature of the spectrum (characteristic of β-MnO_2) is clearly visible. But in the structure, the α lines are maintained. However, there is an admixture of $M_S = -5/2$ and $M_S = -3/2$ levels. Thus it is inferred that the constituent water, which is essential for the stability of the lattice according to the earlier reports,[20] has been partially released, leading to partial collapse of the lattice as revealed by the XRD results (Fig. 10 *vs.* 11), which indicate partial amorphisation. Such

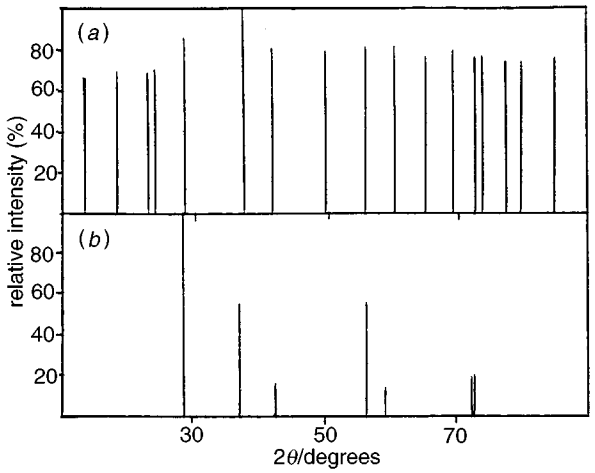

Fig. 10 XRD patterns of cryptomelane (*a*) and pyrolusite (*b*)

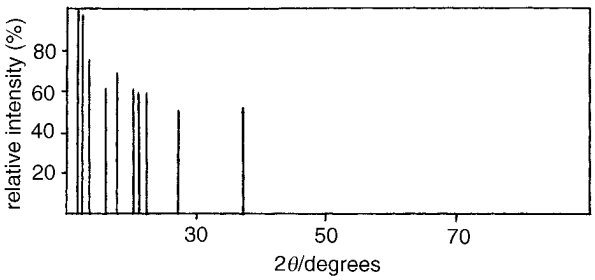

Fig. 11 XRD pattern of cryptomelane after isothermal heating at 100 °C for 2 days

materials may be of interest to electrochemists and battery scientists.

Conclusions

We have detected the manganese spin states in pyrolusite and cryptomelane manganese dioxides at both room- and liquid-nitrogen temperature. From the observation of the room-temperature EPR signals, it can be presumed that Mn^{4+} is present in β-MnO_2 and Mn^{2+} in α-MnO_2. In α-MnO_2 the observed admixture of spectra due to $M_S = -1/2$ and $M_S = +1/2$ is indicative of spin–orbit coupling. Interestingly, at low temperatures, narrowing of the EPR lines is observed for β-MnO_2 and the $M_S = -3/2$ levels in the α form seem to be affected by the changes in crystal field. Isothermal heating of KMn_8O_{16} in air at 100 °C for 2 days affects the manganese negative spin states owing to changes in local environment and oxidation state. The EPR curves have shown evidence that the manganese spin states in cryptomelane are greatly affected by the release of molecular water on heating.

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References

1 *Manganese dioxide batteries*, ed. K. V. Kordesch, Marcel Dekker, New York, 1974, vol. 1.
2 K. V. Kordesch and M. Weissenbacher, *J. Power Sources*, 1994, **51**, 61.
3 P. R. Roberge, M. Farahani, K. Tomanstcher and E. Oran, *J. Power Sources*, 1994, **47**, L13.
4 H. Huang and P. G. Bruce, *J. Electrochem. Soc.*, 1994, **141**, 76.
5 Q. Feng, H. Kanoh, K. Ooi, M. Tani and Y. Nakacho, *J. Electrochem. Soc.*, 1994, **141**, L135.
6 O. N. Khodarev, *Elektrochimiya*, 1991, **27**, 1046.
7 M. V. Ananth, V. Venkatesan and K. Dakshinamurthi, *Mater. Sci. Eng. B*, in the press.
8 R. Giovanoli, *Thermochim. Acta*, 1994, **234**, 303.
9 M. V. Ananth and K. Dakshinamurthi, *J. Power Sources*, 1992, **40**, 355.
10 *ESR Elementary theory and practical applications*, ed. J. E. Wertz and J. R. Bolton, Chapman and Hall, New York, 1986.
11 M. Voinov, *Electrochim. Acta*, 1982, **27**, 833.
12 V. I. Gryaznoc, *Dokl. Akad. Nauk SSSR*, 1958, **121**, 159.
13 T. Ohzuku, M. Kitagawa, K. Sawai and T. Hirai, *J. Electrochem. Soc.*, 1991, **138**, 360.
14 A. P. Pechenyi, M. D. Glinchuk, C. B. Azzoni, F. Scardina and A. Paleari, *Phys. Rev. B.*, 1995, **51**, 12165.
15 T. H. Yeam, S. H. Choh, Y. M. Chang and C. Rudowics, *Phys. Status Solidi B*, 1994, **185**, 417.
16 M. V. Ananth and K. Dakshinamurthi, unpublished results.
17 G. F. Lancaster, *ESR in semiconductors*, Hilger & Watts, London, 1966.
18 H. Tamura, in *Electrochemistry of manganese dioxide and manganese dioxide batteries in Japan*, ed. S. Yoshikawa, U.S. Branch office, Electrochem. Soc. Japan, Cleveland, OH, 1973, p. 189.
19 P. Ruetschi and R. Giovanoli, *J. Electrochem. Soc.*, 1988, **135**, 2663.
20 G. Buttler and H. R. Thirsk, *Acta Crystallogr.*, 1952, **5**, 288.

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