Short communication

Magnetization studies of chemically prepared manganese dioxides

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Abstract

A study is made of the magnetization properties of commercial, chemically prepared, manganese dioxides which are intended for use in dry cells, zinc alkaline cells and magnesium cells. The technique employs a vibrating sample magnetometer and the properties are measured as a function of applied fields at room temperature. A correlation is found between the shift of the (411) XRD peak and the magnetization behaviour. The results indicate that the magnetizability that is observed in these mostly α-phase containing samples can be accounted for by the average Mn–Mn distance and the consequent interactions between manganese spins mediated by O^{2-} and OH^-. Of particular interest to magnetic moments of MnO_2 samples with traces of δ phases is the prediction that the extent of the modification of the birnessite phase has a significant influence. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Manganese dioxide; Magnetization; Crystal structure; Mn–Mn couplings; Phase composition; Battery

1. Introduction

Examination of the magnetic properties of manganese compounds, that were largely ignored until 1950s [1,2], has been gaining momentum recently due the importance of these properties for MnO_2 in assembling batteries [3]. Concerns over future global energy supplies is necessitating the advancement of several types of MnO_2-based batteries. Therefore, the focus has been on developing manganese dioxides with new structures for improved electrochemical output [4]. Amongst the three major sources of manganese dioxide, viz., natural manganese dioxide (NMD), electrolytic manganese dioxide (EMD), and chemically precipitated manganese dioxide (CMD), rapid advancements have been taking place in EMD [5] and CMD [6] as these materials promise to deliver the best performance. Recently, CMDs have out-performed EMDs and are the materials preferred by the battery industry. As there is wide variance in performance, it has become necessary to characterize these CMDs in terms of the important properties. As mentioned above, investigations of the magnetism of these materials are expected to yield interesting and useful results [7]. Such investigations on some popular commercial samples are reported here.

2. Experimental

The five commercial samples chosen for the study were: (A) IC 22 (international common sample); (B) CMD of Japanese Origin; (C) special CMD reported to be equivalent to EMD and of Japanese origin; (D) Sedema CMD; (E) a CMD used in Mg–MnO_2 cells. The magnetic moment (MM) was determined with a vibrating sample magnetometer as described in our earlier reports [8–11]. The XRD patterns were recorded with a JEOL XRD spectrometer using Cu K_α radiation.

3. Results

3.1. Magnetization experiments

The variation in MM with applied magnetic field for the studied samples is shown in Fig. 1. Apart from the five

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commercial samples, pure α cryptomelane and β pyrollusite samples were also investigated for reference. The results are in line with Parida et al. [12] and Fernandes et al. [13] but not with those of Selwood et al. [14]. Samples A, B and C display the linear characteristic of paramagnetic samples, but sample D deviates from this behaviour at higher fields. Also, it displays remarkably reduced magnetic features. Precipitation of ferromagnetic impurities or strong paramagnetic species are seen in samples A and C as compared with sample B. The performance of sample E is close to that of α cryptomelane.

3.2. XRD experiments

The XRD patterns for the five commercial samples are shown in Fig. 2. The following phase analysis can be inferred from the results.

Sample A: not orthorhombic; close to hexagonal; some β microdomains.

Sample B: orthorhombic; some α phases; some modified birnessite.

Sample C: orthorhombic; some α phases

Sample D: not orthorhombic; some modified α phases; structure between orthorhombic and hexagonal; has some birnessite content as revealed from the lines at 7.19 and 3.67 which are diagnostic basal plane reflections for birnessite.
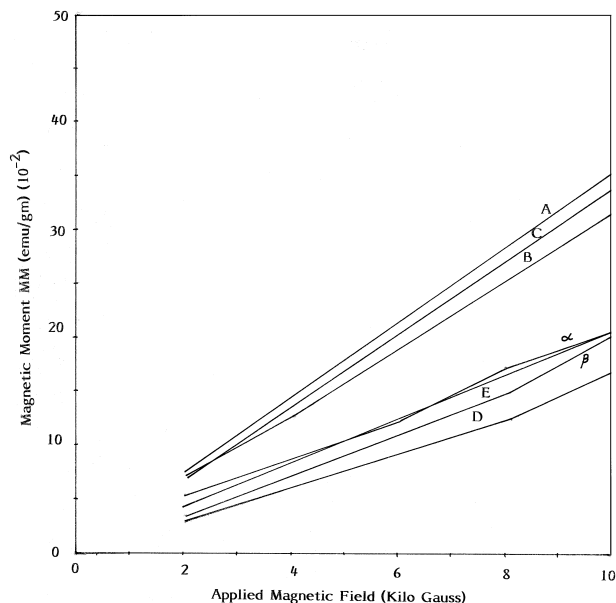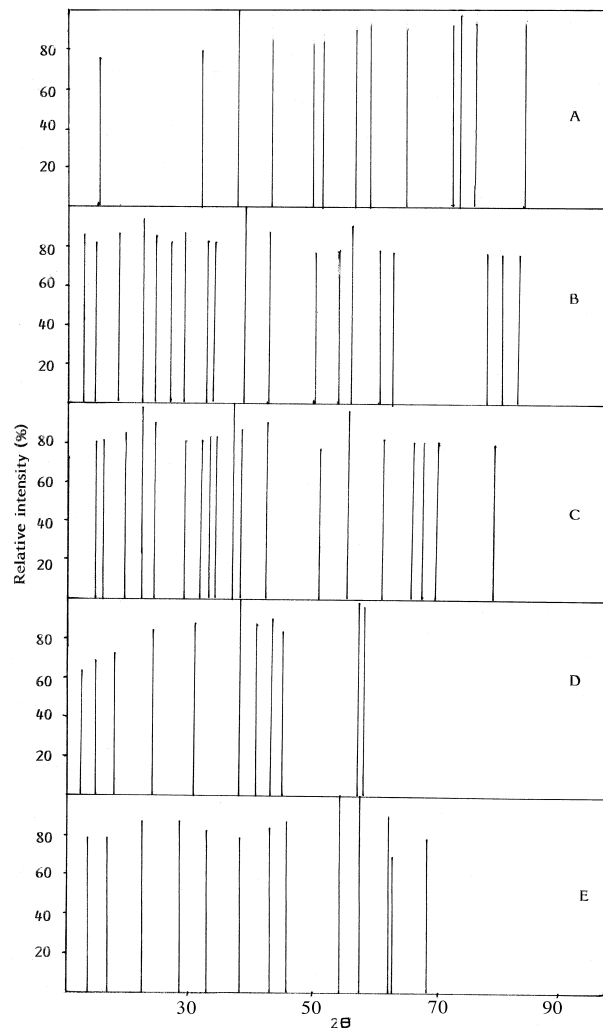
Fig. 2. X-ray diffraction patterns of chemical manganese dioxides.

Sample E: modified α tetragonal and orthorhombic γ phases.

4. Discussion

The investigated samples exhibit different magnetization behaviour. This is to be expected because an appreciable difference in atomic moments occurs between the experimental value of 2.86 μB and the theoretically derived value (based on spin-only relation for 3 unpaired electrons) of 3.88 μB which imparts a distinctive behaviour to MnO_2 on magnetization [15]. This has been explained on the basis of interatomic forces [16] wherein the inter axial 3d orbitals are involved in forming secondary cation-to-cation bonds and only 2.4 of d electrons remain unpaired to Mn^{4+} ions. Amongst the samples, sample A has the highest degree of magnetization, followed closely by samples C and B. Several reasons can be attributed to the present observation. For example, Mn–Mn couplings, especially if ferromagnetic, can impart higher magnetization in samples. The Mn–Mn intermetallic dis-

Fig. 1. Magnetization behaviour of chemical manganese dioxides.

tance across the shared octahedra is around 2.84 Å or the multiple 5.68 Å [17]. The d spacing of 2.84 Å corresponds to diffractions from the (411) plane in a typical α-MnO_2 spectrum [18].

Since sample A has an XRD peak at 2.838, it has Mn–Mn ferromagnetic coupling and the highest magnetic moment. The behaviour of the second highest magnetized sample, sample C, can also be attributed to the presence of Mn–Mn ferromagnetic couplings given its XRD peak at 2.812. Similarly, the magnetization behaviour of samples B, E and D can be explained in terms of Mn–Mn couplings from their XRD peak values of 2.786, 2.7789 and 2.910, respectively. Thus, it is seen that any deviation from an ideal Mn–Mn approach of 2.84 Å promotes anti-ferromagnetic coupling been the Mn atoms and results in reduced magnetization. This is because a too close Mn–Mn approach effects the anti-ferromagnetic coupling and a too large Mn–Mn approach results in paramagnetic couplings.

The second reason for the presence of higher magnetic features in chemical manganese dioxides could be due to a lengthening of the Mn–O bond [19,20] or a diminished paramagnetic neighbourhood. In other words, the effect of dispersity may also be partially responsible for higher magnetic moments. This has been explained from possible relaxation of the covalent bond between Mn and O in (MnO_6) octahedra in highly dispersive MnO_2 gel. The average Mn–O distance has been reported to be 1.88 Å [21]. From the XRD experimental results, the bond lengths for samples A, B and C could be arbitrarily put at 1.836, 1.883 and 1.826 Å, respectively. It can be easily seen that the observed magnetization behaviour cannot be explained solely on the basis of Mn–O bond lengths. This is to be expected, however, as a lengthening of the Mn–O bond has been reported to occur in δ-MnO_2 and some of the investigated polymorphs contain only minor δ-MnO_2 phases.

The third reason could be due to non-stoichiometry. The magnetic susceptibility of MnO_2 has been reported to increase with Mn^{2+} and Mn^{3+} contents. In fact, EXAFS measurements have shown that the cations are bound in a birnessite structure, in hydrates of 7 Å phyllomanganates, and in layered structures with stacking disorder between the 2D sheets of edge-shared [MnO_6] octahedrals separated by 10 Å [22]. Intermediate layers contain sheets of H_2O molecules or OH^- ions bonded to the [MnO_6] octahedra layer by cations. Thus, alternately a rough estimate of the Mn^{2+} and Mn^{3+} ions has been attempted from a study of the d spacings around 7 Å in samples with δ-phase. The maximum value of the d spacings is observed at 7.19 and 7.019 Å for samples D and B, respectively. The observed magnetization behaviour can be explained to some extent on the intensity of this peak. Nevertheless, the present observation cannot be explained on these grounds for all the samples as all of them do not contain the δ-phase.

The fourth reason could be due to the presence of Na^+ or K^+ ions. Na^+-containing samples are known to exhibit a higher magnetic susceptibility [23]. The highest magnetic susceptibility observed for sample A can be attributed to the presence of 160 ppm of Na^+.

The fifth reason could be due to the nature of phase composition. As mentioned earlier, the presence of δ-phase is identified in samples B and D. The observed variance in the magnetic moment for the four samples can be attributed to the occurrence of the δ-phase as the latter has been reported to possess a magnetic susceptibility that is higher than that of the various phases (α, β, γ, etc.) of MnO_2. It is found, however, that the degree of sub-modification of δ-phase plays the deciding role in altering the magnetic moments. Also, in general, it appears that closely packed crystallites exhibit higher magnetic moments which again supports the above-mentioned predominant influence of Mn–Mn couplings on the magnetic moment of the samples.

5. Conclusions

Magnetism in chemically prepared manganese dioxides intended for battery applications is predominantly influenced by the extent of Mn–Mn couplings in the samples. Also, the amount and modified nature of the δ-phase in the samples has a significant effect on the magnetization behaviour.

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