

Short communication

Distortion of MnO_6 octahedra and electrochemical activity of Nstutite-based MnO_2 polymorphs for alkaline electrolytes—an FTIR study

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Abstract

Infrared fourier transform (FTIR) spectroscopic analysis of four commercial manganese dioxides having applications in alkaline batteries is reported. These samples of different alkaline activity have Nstutite or $\gamma\text{-MnO}_2$ as the major phase. With respect to the interaction of Mn with OH^- and other groups, the development of weak bands around 1363 cm^{-1} represents the variation in discharge performance. Significant changes are seen in the MnO_6 octahedral arrangement from sample to sample by examining the spectra in low-frequency regions. Distortion of MnO_6 octahedra by the constituent water promotes the electrochemical behaviour. In general, the alkaline electrochemical activity of Nstutite MnO_2 samples can be understood from their infrared spectra. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Fourier transform infrared spectroscopy; Manganese dioxides; Electrochemical activity; Nstutite phase; Constituent water

1. Introduction

Manganese dioxide is an important active material which is used widely in the battery industry because of its many applications in different types of power sources such as dry cells (alkaline primary and rechargeable versions) and magnesium- and lithium-based cells. Manganese dioxide is a complex material and exists in different crystallographic structures that enables it to exhibit a varied battery performance in different systems. It is now well known that the electrochemically active Nstutite or $\gamma\text{-MnO}_2$ phase, usually employed for alkaline battery electrode fabrication, contains ‘structural water’ [1]. Nstutite MnO_2 is an intergrowth of ramsdellite (α) and pyrolusite (β) manganese dioxides (Fig. 1). The location of this structural water has warranted detailed studies. Among the different battery applications of MnO_2 , the latest popular application is in alkaline batteries due to a strong market presence in pagers

and photoflash sectors [2]. Therefore, MnO_2 samples intended for use in alkaline electrolytes require intensive characterization to optimize their performance. In general, several investigations have been performed on manganese dioxides in terms of crystallographic structure [3], chemical composition, thermal behavior [4], magnetic properties [5], electrical resistivity [6]. Among the various investigation tools like X-ray diffraction, microscopy, thermal analysis, magnetic susceptibility, inelastic neutron scattering [1], magnetic resonance [7,8], infrared spectroscopy [9] is a simple and useful technique.

Infrared spectra of manganese dioxide can yield much valuable information. For example, they can be used to locate the presence of OH^- groups as well as H_2O molecules that may be present as bound water within the crystal structure [9]. The presence is usually indicated by absorption around 3400 and 1620 cm^{-1} . Also, the different crystalline phases can be identified to some extent. For example, all $\gamma\text{-MnO}_2$ samples show an absorption around 1620 cm^{-1} , which may be attributed to the O–H bending mode of vibration. The adjacent weak absorptions may indicate an increased degree of freedom for the bending vibrational mode of the O–H bond due to the presence of the γ phase. The strong absorption in the range 2000 to

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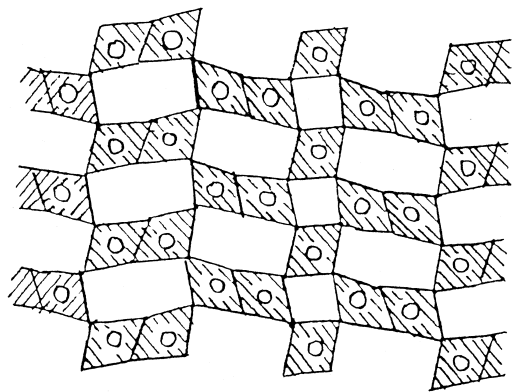


Fig. 1. Crystal structure of Nstutite—an intergrowth of ramsdellite and pyrolusite manganese dioxides.

900 cm^{-1} may be due to the different degree of hydrogen bonding in the samples. The broadening of the peak in the range 600 to 515 cm^{-1} may indicate the presence of the γ phase. The electrochemical activity can be inferred to some extent by the shift in the Mn–O absorption frequency minima. In the present study, an attempt has been made to investigate the performance of four types of commercially available manganese dioxide containing Nstutite structure. This has been achieved by means of infrared Fourier transform (FTIR) analysis.

2. Experimental

Four samples of MnO_2 suitable for use in alkaline electrolytes were examined. Those labelled A, B and C were of electrolytic origin, while sample D was prepared chemically. For the measurement of alkaline battery activity, 0.40 g of MnO_2 was mixed with 0.10 g of KS 44 graphite powder and compacted on perforated nickel meshes ($1.5 \times 1.5\text{ cm}^2$) with PTFE binder. A ‘Kuralon’ separator was used. Perforated zinc sheets served as the anodes. Thirty-one percent KOH (w/v) was used as the electrolyte. The cell was discharged at 25 mA and the discharge duration was continued up to a cut-off voltage of 0.9 V per cell.

FTIR measurements were made on the above samples with KBr pelletisation in the range 400 to 4000 cm^{-1} . A Perkin Elmer instrument was used for these measurements. Efforts were taken to ensure that the FTIR spectra of MnO_2 samples were not influenced by sample preparation. Samples of the same particle size were taken to eliminate the effects due to particle size on the relative intensities and the shape of the absorption features. Each FTIR measurement was repeated to ensure reproducibility of the spectra and homogeneity of the sample. The absence of nitrate and carbonate was confirmed by analysis in order to obtain correct interpretation of FTIR spectra, X-ray diffractograms were taken by means of a JEOL XRD instrument with $\text{CuK}\alpha$ radiation.

3. Results and discussion

3.1. Electrochemical activity

Discharge curves for the various samples are shown in Fig. 2. The electrochemical activity of the samples increase in the order $A > B > C > D$.

3.2. X-ray diffraction

The samples exhibit different XRD patterns (Fig. 3) even though they display Nstutite phase, as revealed by the presence of the peak at a ‘d’ spacing of $\sim 4\text{ \AA}$. Earlier studies in the literature have suggested that either the γ phase or its modified version, viz., the ϵ phase, promotes electrochemical activity in alkaline solutions. Recently, however, the layered δ phase components (Fig. 4) have also been found [10] to increase discharge capacity. The presence of such layered phase can be detected in samples A, B and C, as evidenced by the peak which corresponds to a ‘d’ spacing of 7 \AA . An examination of the XRD pattern itself is not sufficient, however, to explain the observed variation in discharge capacity in terms of differences in phase composition. Nevertheless, based on the intensity and the width of the peaks, it can be concluded that crystallinity decreases partially in the order $A < D$.

3.3. Fourier transform infrared spectroscopy

The FTIR spectra of the four samples (A to D) are shown in Fig. 5 to 7, i.e., in three regions of interest. The spectra in the range 4000 to 3000 cm^{-1} furnish information on the constitutional water, if any, present in the sample. The interactions between manganese and the constituent species are revealed in the range 2500 to 1000 cm^{-1} . The MnO_6 octahedral structure can be examined by analysing the spectra in the low-frequency region (1000 to 400 cm^{-1}).

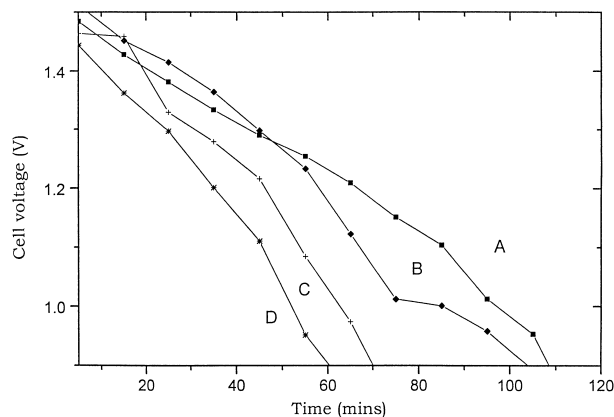


Fig. 2. Electrochemical activity of manganese dioxides in 31 wt.% KOH.

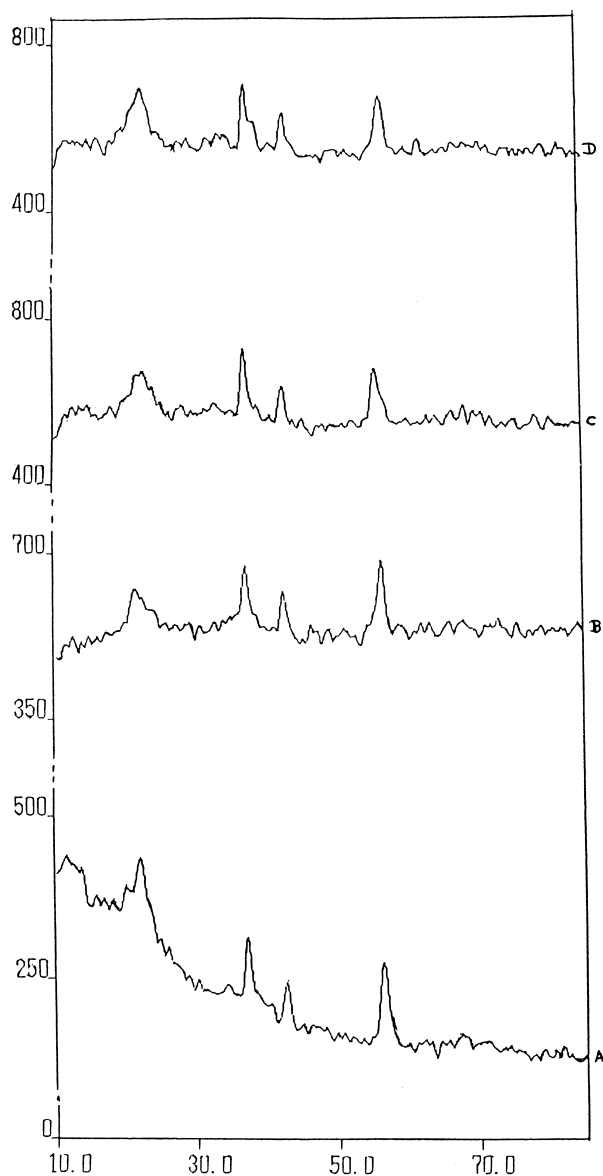


Fig. 3. X-ray diffraction pattern of MnO_2 samples.

3.3.1. Incorporation of water

Among the four samples studied, the peak for constitutional water is well resolved only in sample A. A literature survey indicates that in hydrous samples, the band at frequency 3400 cm^{-1} is representative of the O–H stretching vibration. In sample A, however, an IR band occurs at 3449 cm^{-1} , i.e., at a higher energy. In sample B, some

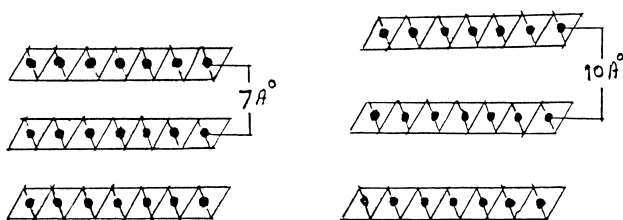


Fig. 4. Crystal structure of layered manganese dioxide.

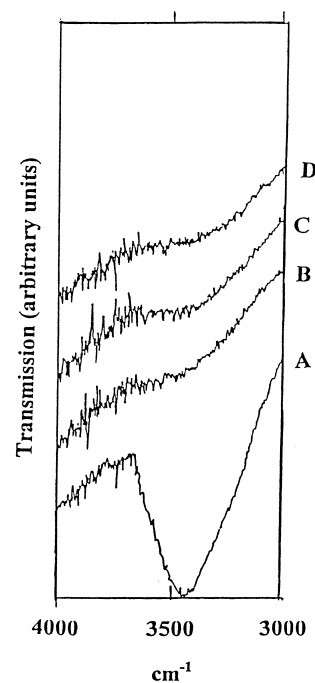


Fig. 5. FTIR spectra revealing information on constitutional water in MnO_2 samples.

weak absorption occurs at $\sim 3600\text{ cm}^{-1}$ (the bands are not distinct). Samples C and D also show negligible absorption in this range. Although all the samples exhibit comparable battery activity, it is interesting to note that the hydrated nature, as evident by the absorption around 3400 cm^{-1} , does not appear to influence strongly the alkaline battery activity. A further notable point is that the activity increases with the slope of the curve (viz., increased intensity of absorption), i.e., the base line.

3.3.2. Interaction of Mn with OH and other groups

The bands at 1593 , 1363 and 1050 cm^{-1} (Fig. 6) represent the vibration due to interaction of Mn with surrounding species such as OH, O, H^+ and K^+ . Previous workers [11] have found that the activity increases with the intensity of these peaks. It is also seen here that the high intensity peak at 1593 cm^{-1} appears in the IR spectra of high-performing samples. It has been reported [11] that in hydrous MnO_2 samples, this peak appears at 1510 cm^{-1} . The high frequency shift in the present case reveals the strongly bonded nature. The 1280 cm^{-1} vibration observed in hydrous MnO_2 [11] also shifts to a higher frequency region (around 1363 cm^{-1}) in the studied samples. The nature of absorption around 1593 cm^{-1} does not seem to exert much influence on the activity.

Typical hydrous MnO_2 is characterized by three bands, viz., at 1510 , 1280 and 1050 cm^{-1} [11], while $\gamma\text{-MnO}_2$ exhibits clear absorption at 1620 cm^{-1} [9]. These four bands are normally attributed to O–H bending vibrations combined with Mn atoms. In the present case, however, all samples display absorption at higher frequencies, viz., at

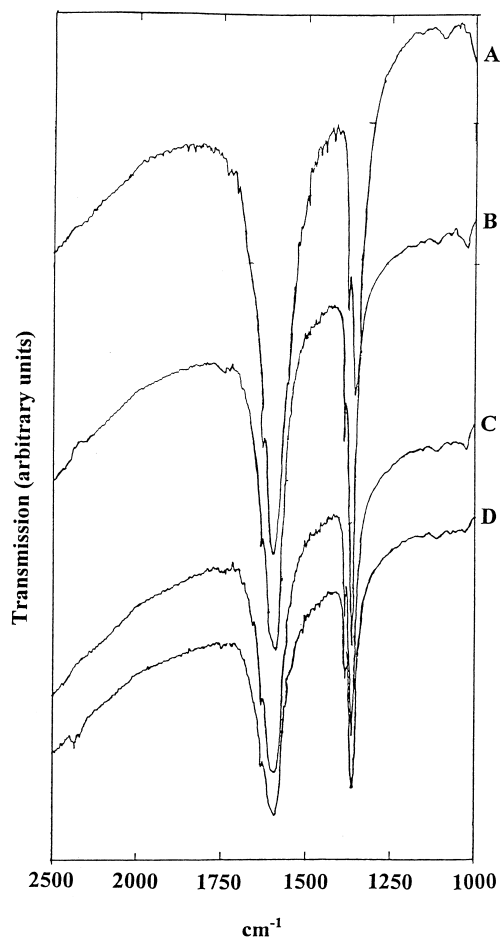


Fig. 6. FTIR spectra indicating the interaction of Mn with OH and other species.

around 1593 and 1363 cm^{-1} , with some additional weak absorption at around 1384 cm^{-1} . Since all samples are treated with alkali, these bands can be assigned to bending vibration of the hydroxyl group contained in the alkali. The absorption at 1620 cm^{-1} is usually associated with water of crystallization, but the presence of weak O–H stretching absorption in samples B, C and D and the occurrence of new vibrational bands at 1593 and 1363 cm^{-1} clearly indicate different linkage of –OH groups in the MnO_2 crystal structures studied here. This is expected because of the presence of other phases (e.g., $\gamma\text{-MnO}_2$) and the alkali content in the samples. Nevertheless, the absorption in this region does not seem to influence battery activity to any great extent. Instead, the development of small peaks at around 1363 cm^{-1} are indicative of the slight variation in activity.

The width between the peaks determines the battery activity. It is noted that the shift of the 1363 cm^{-1} peak to the low-frequency region enhances the activity. Sample A has been found to be the most active amongst the samples studied. For this sample, the intensity variation in the 1593 and 1393 cm^{-1} peaks is greatest and the degree of absorption at 1593 cm^{-1} , which can be associated with alkali

content, determines the activity of the MnO_2 . The intensity and the sharpness of the peak at 1050 cm^{-1} also appears to influence the alkaline battery activity, which agrees with the earlier observation.

3.3.3. MnO_6 octahedra arrangement

As noted above, the IR bands in the region 1000 to 400 cm^{-1} (Fig. 7) reveal information about MnO_6 octahedra. Among the three different regions of the IR spectrum, a major difference from sample to sample has been witnessed only in this region. It is also found that the phase composition of the samples appears to influence strongly the IR spectra in this region. Initial examination of the spectra reveals that the MnO_6 octahedra has been distorted due to constitutional water in highly performing samples. The greater the distortion, the higher the electrochemical activity in alkaline media. In sample A, sharp peaks are present at 1048 , 675 and 424 cm^{-1} . A weakly developed doublet and a feeble doublet occur in the $600\text{--}540$ and $460\text{--}440\text{ cm}^{-1}$ regions, respectively. The normal pattern as reported in the literature does not appear here, although some similarities are observed in the spectra of the C and D samples. Sample B displays absolutely a different structure—no sharp peaks can be seen. Moreover, the weakly developed doublet in the 600 to 540 cm^{-1} region seen in

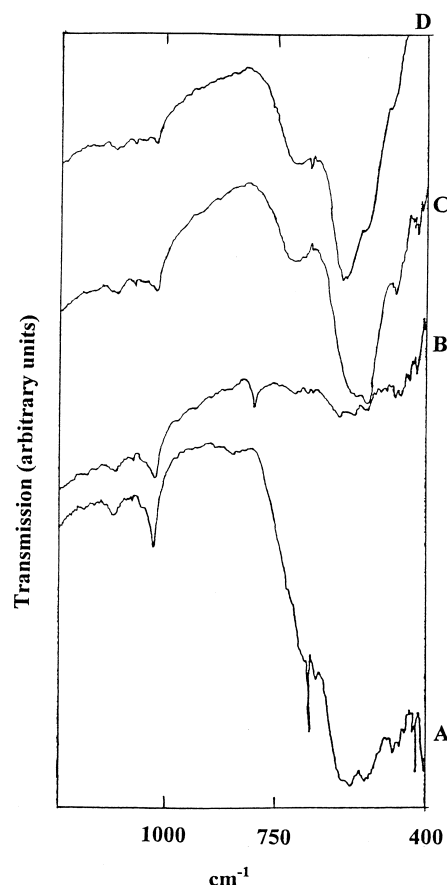


Fig. 7. FTIR spectra representing the MnO_6 octahedral arrangement.

the spectrum of sample A has transformed into a triplet. On the other hand, the feeble doublet in the region 460 to 440 cm^{-1} is retained as in sample A. It can be stated that in sample B distortion of MnO_6 octahedra has occurred. Except for some minor modification, the IR pattern of samples C and D remain similar to those reported in the literature for the Nstutite MnO_6 octahedra. Thus, IR spectra reveal that distortion of MnO_6 octahedra decreases in the order $A > B > C > D$, which is in line with XRD results. The distortion of MnO_6 octahedra and the resultant partial amorphisation is responsible for the increased alkaline battery activity.

4. Conclusions

The infrared spectra of commercial Nstutite-based manganese dioxides for alkaline electrolytes show that the electrochemical activity is not dependent on the constitutional water content but rather on its influence on the lattice structure. In highly performing samples, the distortion of the MnO_6 octahedra by the presence of water is maximum. The distortion of MnO_6 octahedra occurring in the samples is supported by the crystallographic structure.

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