

Influence of aluminium doping on the electrochemical behaviour of manganese dioxide

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Abstract

The electrochemical behaviour of laboratory prepared manganese dioxide with different additions of aluminium has been investigated. The findings have been compared with the ones found for commercial samples. All samples have been submitted to X-ray diffraction measurement. The electrochemical reduction has been carried out in 1 and in 9 M KOH electrolytes, by means of slow rate voltammetric tests. Interesting correlations have been found between the results of the physico-chemical characterisation and the electrochemical behaviour. Among other beneficial effects, aluminium seems to improve the quality and uniformity of the contact between the dioxide surface and graphite, thus increasing the conductance of the mass and the amount of dioxide available for the reduction. Examination of the samples surface has revealed that such effect is tied to the specific kind of morphology induced by aluminium. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

Manganese dioxide has been widely investigated for more than a century since its utilisation in the Leclanché battery and for almost 40 years after the introduction of alkaline manganese batteries. In spite of the early and extensive research which has been carried out, important features concerning the electrochemical reduction of MnO_2 remained unclear for a long time. One of the reasons of such difficulty lies in the fact that the more electrochemically active forms, γ - and ϵ - MnO_2 , present highly defective structures with large deviation from stoichiometry, which are indeed responsible for such a good behaviour, but make the characterisation of those species very hard, both for the quality of the X-ray diffraction patterns and for the scarce reproducibility of electrochemical reduction tests unless strictly defined and controlled experiments are carried out.

After the work by Brenet [1], who was the first to interpret the initial electrochemical reduction by means of insertion of protons in the MnO_2 structure, and the work by Ruetschi [2,3] who proposed a model accounting for non-stoichiometry of electrochemically prepared manganese dioxide (EMD) on the basis of Mn^{4+} vacancies, some of the

unsolved questions received an answer and the idea of an electrochemical reduction step through a homogeneous phase was widely accepted.

Many subsequent investigations have proved the importance of the above approach but at the same time pointed out that the complexity of the electrochemistry of γ - and ϵ - MnO_2 had not yet been elucidated. Chabre and Pannetier [4] in their recent review remark that only after the mid-1980s the interesting structure features of γ - MnO_2 discussed by De Wolff [5] have been considered when interpreting the electrochemical properties of the dioxide. Pannetier [6] improved the description of the γ - MnO_2 structure by considering also the presence of microtwinning defects. This new structural model has been used [7,8] to interpret some features of the X-ray patterns and their correlation with the electrochemical behaviour of the dioxide.

To achieve the rechargeability of the manganese dioxide electrode, different areas must be further investigated, the improvement of the electrochemical reactivity of the dioxide during the so called reduction in the homogeneous phase on one hand, and the chemical or structural modification of γ - MnO_2 on the other hand. Recent contributions [9–12] to the problem of manganese dioxide cyclability pointed out the importance of locating appropriate potential intervals and discharge/charge rates for cycling. There are indeed examples showing that good cycling capabilities can already be achieved [13] at the commercial level.

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One of the most widely used means to improve the performance of the MnO_2 system is that of “doping” the dioxide with some suitable substance. The ways of modifying MnO_2 are very numerous and vary, among others, according to the application aimed as proved by some examples. The enhancement of the electrochemical reactivity of the dioxide has been obtained by Brenet [14] by introducing suitable cations directly during the MnO_2 preparation. Skowronsky [15] used a mixed cathode formed by dioxide and graphite/chromium trioxide intercalation compound to increase the cathode capacity. The improvement of the rechargeability in secondary cells has been studied among others by Dzieciuch et al. [16] using cathodes in which bismuth and lead compounds were present. Another problem of rechargeable systems containing MnO_2 , the formation of soluble manganates causing loss of active material has been overcome by adding or complex oxides of various metals by coprecipitation to the MnO_2 [17]. More recently, Jantscher et al. [18] prepared and studied barium and barium/titanium doped EMD. By applying abrasive stripping voltammetry, they found that barium doped EMD compared well with the commercially available material and that barium/titanium doped EMD exhibited a superior charge retention and rechargeability when compared to undoped material. Sharma et al. [19] performed a study doping natural manganese dioxide (NMD) inserting an Mo based oxide. The results allowed to conclude that the doping upgraded the properties of NMD for its application as cathode material in dry batteries.

This paper, following some previous studies [20,21] on the electrochemical reduction of manganese dioxide, presents the results obtained on the investigation of laboratory prepared manganese dioxides, pure and modified by adding different amounts of aluminium during the preparation process. The electrochemical behaviour has been tested in 1 and in 9 M KOH electrolytes, by performing slow rate voltammetric tests on powder samples containing acetylene black. Some interesting correlation between structural features of the various samples and their electrochemical behaviour are pointed out. The method of preparation was chosen for its low technological complexity and cost in comparison with the commercial chemical and electrochemical preparations. The choice of aluminium as a doping element has been done on the basis of a limited preliminary screening, some suggestion from the literature [14,21] and by considering the favourable charge/radius ratio of Al(III) which is close to that of Mn(III). The electrochemical behaviour of commercial CMD and EMD samples has been also investigated to get the real performance of laboratory samples by comparison with commercial ones.

2. Experimental

Different manganese dioxide samples have been tested in the present work, including two commercial products,

namely CMD (Sedema) and EMD (Delta), together with a series of laboratory prepared manganese dioxide samples formed in the presence of variable amounts of aluminium added as nitrate in the preparation process according to the procedure outlined below. Analytical grade reagents and bidistilled water were used for the chemical synthesis.

2.1. Preparation of the laboratory samples

Pure and Al containing samples were prepared by a modified chlorate method [22,23]. Pure manganese dioxide powders were obtained by adding KClO_3 (0.17 M) and HNO_3 (4 M) solutions to $\text{Mn}(\text{NO}_3)_2$ (0.57 M) solutions under stirring conditions and at a constant dripping rate ($1.3\text{--}2.5\text{ cm}^3\text{ min}^{-1}$). The temperature was maintained at 85°C . After 5 h of reaction the solutions were dried at 150°C . The pure sample is labelled MNAL0.

Al containing samples were prepared by adding different quantities of $\text{Al}(\text{NO}_3)_3$ directly in the $\text{Mn}(\text{NO}_3)_2$ solutions. The additions of $\text{Al}(\text{NO}_3)_3$ were 0.5, 5 and 10 wt.% and the resulting samples have been labelled MNAL05, MNAL5 and MNAL10, respectively.

In order to test the influence of the preparation procedure, one Al containing sample was obtained by reversing the order of the reagents addition in the preparation batch. This sample was prepared by introducing 0.5 wt.% of $\text{Al}(\text{NO}_3)_3$ in the batch and has been labelled MNAL05B.

2.2. Structural and morphological characterisation

The X-ray powder diffraction patterns were collected by means of a Philips PW1710 diffractometer, with a Cu anticathode and monochromator. Measurements were performed in the θ range $5\text{--}35^\circ$, with a step scan of $0.01^\circ\theta$ and a count time of 15 s per step, using auto-divergence slit. The morphology of the samples was examined by means of scanning electron microscope observations and granulometric measurements were performed for all studied powders.

2.3. Electrochemical measurements

The working electrode was purposely designed and consisted in pvc body containing a platinum disk which supported the MnO_2 pellet. This pellet was obtained by mixing MnO_2 powder and acetylene black in a mortar in the weight ratio 1:8. The powder mixture was then added with a suspension of teflon in ethanol. After outgassing the alcohol the pellet was positioned on the Pt disk and fixed by means of a porous glass disk. The electrolytic cell contained also a Pt gauze-counter electrode and a Hg/HgO reference electrode. All reported potential values are referred to Hg/HgO electrode in the same test solution. KOH of 1 M and solutions of 9 M were prepared using analytic grade reagents and bidistilled water. All electrochemical tests have been performed at 25°C .

The electrochemical reduction of both commercial and laboratory prepared samples was investigated by linear sweep voltammetry (LSV), carried out in 1 M KOH solutions with a sweep rate of $30 \mu\text{V s}^{-1}$. In order to test both reducibility and recyclability of studied manganese dioxides, cyclic voltammeteries (CV) were carried out in 9 M KOH solutions; the sweep rate was again $30 \mu\text{V s}^{-1}$. Electrochemical tests were performed using AMEL SYSTEM 5000 apparatus.

3. Results and discussion

3.1. Diffractometric measurements

The most common forms of MnO_2 (usually known as γ - and/or ε - MnO_2) are all related to the mineral structures known as ramsdellite and pyrolusite. The first one is an orthorhombic modification of MnO_2 which is a rare mineral. Pyrolusite is tetragonal and isostructural with rutile (TiO_2) and is constituted by single chains of edge sharing MnO_4 octahedra connected through corner sharing, with neighbouring chains [24]. In both structures Mn^{IV} results coordinated by a slightly distorted oxygen octahedra, while the edge-sharing octahedra chains run parallel to c_0 direction in both structures.

The electrochemically active MnO_2 is indeed based on an highly defective ramsdellite structure, the type and amount of defects being related to the preparative route employed. By examining the reciprocal lattice, it can be shown that the points corresponding to ideal ramsdellite planes become elongated ellipsoids in a defective lattice, therefore inducing specific line broadening and peak shifts in the X-ray diffraction patterns of γ - and/or ε - MnO_2 samples.

All MnO_2 samples studied were submitted to X-ray profile analysis. The results have been reported in Fig. 1. It is clearly detectable the overall similarity between the

diffractograms of the laboratory prepared samples and that of EMD sample. Only MNAL05B sample, the one obtained by reversing the order of the reagent addition shows a pattern similar to that of CMD.

The EMD sample cannot be indexed with an orthorhombic unit cell; the peaks can be indexed with an hexagonal cell having $a_0 = 2.77 \text{ \AA}$ and $c_0 = 4.24 \text{ \AA}$, leaving, however, unindexed the strong and wide peak at $\theta = 10.8^\circ$ (corresponding to the 110-line of the ramsdellite structure) and other minor peaks. The JCPDS Card closest to this pattern is card # 30-820 (MnO_2 — akhtenskite syn.) [25]. In this card, the line around $\theta = 10.8^\circ$ is unindexed, but reported with a weak intensity of 1%. This akhtenskite phase belongs to the structure-type Fe_2N and consists, therefore, of an hexagonal close packing of O_2 -ions with half of the octahedral sites randomly filled with Mn^{IV} atoms [5].

The pure MNAL0 sample showing a structure similar to that of EMD, contains also impurities due to the presence of α -phase (kriptomelane). All Al containing samples present a EMD-like structure with a different amount of defects, nevertheless, MNAL05, MNAL5 present a structure with some reflections typical of ramsdellite. More detailed data on the analysis of diffractometric results are reported elsewhere [8,26].

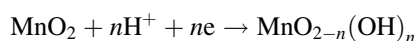
The CMD Sample contains significant amounts of De Wolff and microtwinning faults, as indicated by diffuse line broadening; however, the orthorhombic line splitting of the reflections h21/h40 is still evident, therefore this sample has not reached the apparent hexagonal symmetry of sample EMD. It belongs, thus, to type-II MnO_2 , according to Pannetier [27], with tetragonal structure.

The inversion of reagents addition during the preparation leads again to a CMD-like structure as shown by X-ray pattern of MNAL05B sample.

3.2. Electrochemical measurements

The voltammograms of Fig. 2a and b are related to the reduction process in 1 M KOH for the pure and the doped oxides, respectively. No oxidation voltammogram is reported in the plot as no anodic process occurs in the scanned potential range.

In KOH solutions, the first step of the electrochemical reduction leads to the formation of groutite (α - MnOOH) [4]. This is generally considered as a homogeneous process, because the potential decreases continuously with the progress of the reaction. The reduction process occurs through the insertion of protons:



Only this reduction reaction apparently occurs when the process is carried out in 1 M KOH.

The anodic voltammetric curves in 1 M KOH have not been reported since no significant anodic oxidation is detected in the considered potential range. This can be due to some specific features of the reduction products

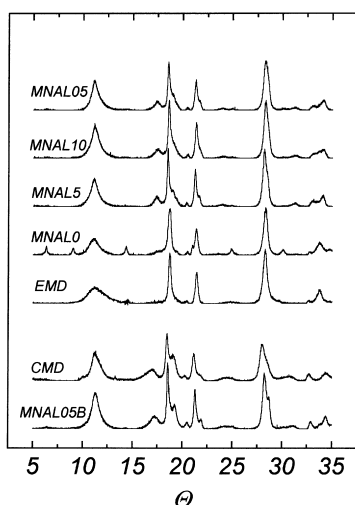


Fig. 1. X-ray diffraction pattern for considered samples.

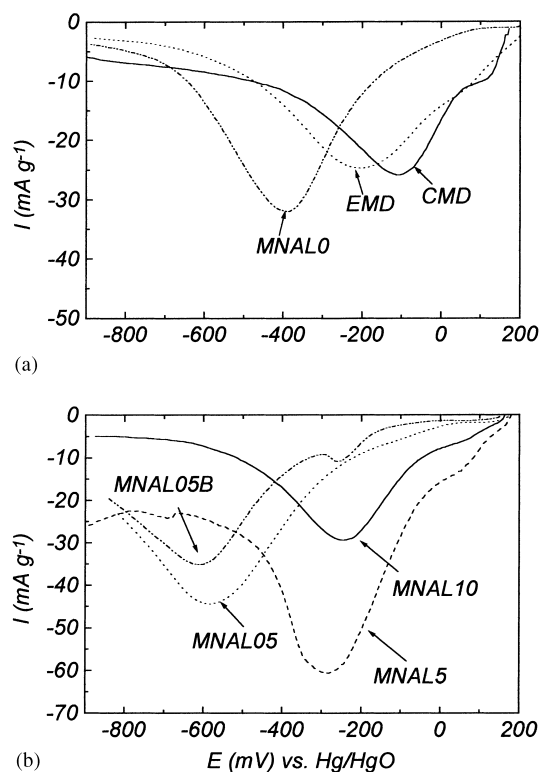


Fig. 2. Linear sweep voltammetry of MnO_2 pure samples (a) and Al containing samples (b) in 1 M KOH. Sweep rate $30 \mu\text{V s}^{-1}$.

which form on the oxide particles. For example, it was shown [20] that in acidic solution the MnOOH layer inhibits the complete reduction of MnO_2 and it cannot be easily re-oxidised.

In Fig. 2a, each curve shows one broad peak whose potential shifts towards negative values in the order $\text{CMD} < \text{EMD} < \text{MNAL0}$. In the case of CMD sample, a shoulder at about 50 mV is present.

The results obtained for the commercial samples are in agreement with those reported in the literature [4,7,8]. According to the interpretation given by Amarilla et al. [11], the major peak has been attributed to the reduction of manganese in ramsdellite blocks. In the case of CMD, a shoulder is detectable that can be ascribed to the reduction of surface states. Such a correlation is also observed for Al containing samples. In fact MNAL05B, with exactly CMD-like structure, presents the same shoulder. X-ray pattern of MNAL10 shows a weak line splitting of the reflections $h21/h40$, in this case a scarcely defined shoulder is present.

If we take into account the electrochemical activity of the samples, defined as the capacity of forwarding the highest quantity of energy at the highest potential value, we see that the pure laboratory oxide (MNAL0) is unattractive for practical applications. It reduces in fact at more negative potentials than the commercial samples. It must be considered, nonetheless, that its preparation was chosen because it is a comparatively easy and inexpensive method to produce $\gamma\text{-MnO}_2$.

The presence of Al (Fig. 2b) affects more or less markedly the position and the intensity of the reduction peaks according to the added quantity. The samples prepared with 0.5 wt.% $\text{Al}(\text{NO}_3)_3$ have peaks shifted to lower potential values showing a lower electrochemical activity than the corresponding pure oxide. The reduction behaviour of MNAL10 is fairly comparable to that of EMD. In this case the addition of aluminium makes the performance of the laboratory prepared MnO_2 very close to that of the commercial products. The oxide prepared with 5 wt.% of $\text{Al}(\text{NO}_3)_3$, MNAL5, show the best performance from the electrochemical point of view, having the peak near that of the commercial samples but at a much higher intensity.

The voltammetric curves for Al added samples put in evidence that the influence of aluminium is not directly related to the quantity added. In MNAL05 the reduction peak is located at more negative potentials, while in the case of MNAL10 the peak is shifted at higher voltages with respect to the MNAL0 while MNAL5 shows the least variation in potential but the highest one as for peak current density.

In 9 M KOH the oxidation process is well evident, so that cyclic voltammetries (two cycles) have been carried out in order to obtain some information on the cyclability of the studied systems. Some of the voltammetric cycles for the pure Mn dioxides are reported in Fig. 3: CMD (EMD behaves very similarly to CMD) and MNAL0. In Fig. 4

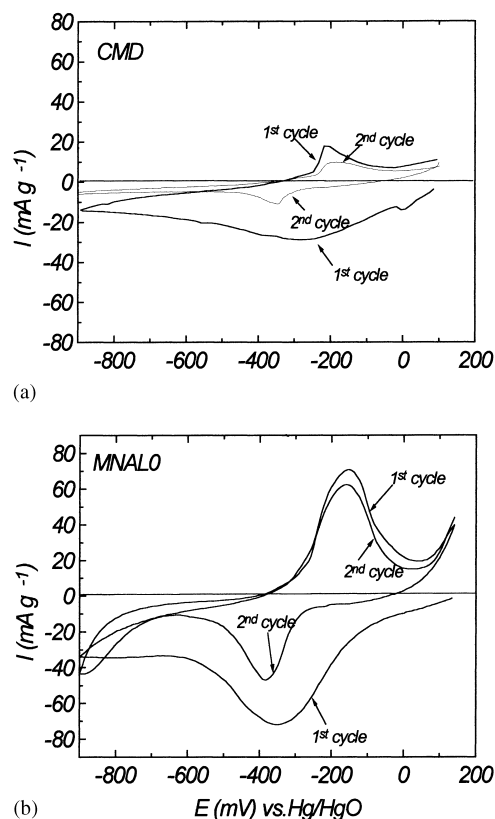


Fig. 3. Cyclic voltammetries of MnO_2 pure samples (CMD and MNAL0) in 9 M KOH. Sweep rate $30 \mu\text{V s}^{-1}$.

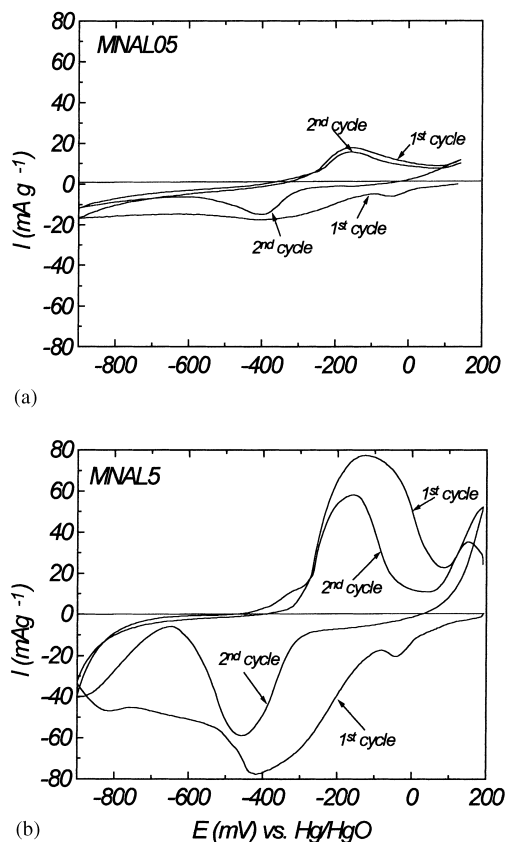
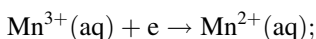


Fig. 4. Cyclic voltammeteries of MnO_2 Al containing samples (MNAL05 and MNAL5) in 9 M KOH. Sweep rate $30 \mu\text{V s}^{-1}$.

are reported the curves for MNAL05 and MNAL5 as examples of low and high capacity cycles.

Some features are common to all samples. The first reduction gives a very broad peak at a potential ranging between -300 and -400 mV, while the following oxidation step shows two convoluted peaks between -300 and -200 mV. At the second cycle the reduction peak appears to be more narrow and both the anodic and cathodic capacity are reduced with respect to the first cycle. The shoulder at about 0 mV in the case of the first reduction of the CMD sample is still present and disappears during the second reduction step.

In 9 M KOH a further reaction, corresponding to a two-phase equilibrium ($\text{MnOOH}/\text{Mn}^{3+}$), takes place. Due to the high basicity of the electrolyte, the dissolution of the Mn^{3+} species, its reduction and precipitation of $\text{Mn}(\text{OH})_2$ occur:



In 9 M KOH solutions the ample and not well defined reduction peak hides the two reduction steps. The broadening of the peak may be a consequence of the rather high value of the potential sweep rate. It can be observed that the position of peaks is nearly the same for all the samples. The

Table 1

Specific capacity (in C g^{-1}) during reduction (Q_{red1} and Q_{red2}) and oxidation (Q_{ox1} and Q_{ox2}) at the first and second cycles for the various samples considered

	Q_{red1}	Q_{ox1}	Q_{red2}	Q_{ox2}
MNAL0	239	148	105	105
CMD	63	22	16	13
EMD	125	80	34	28
MNAL05	40	27	21	21
MNAL05B	120	120	80	80
MNAL5	286	178	134	112
MNAL10	13	10	7	7

peak values are in agreement with literature data. In this, electrolyte samples exhibiting CMD-like structure present the initial shoulder as already reported for the tests carried out in 1 M KOH (Fig. 3).

On the anodic branch of the voltammetric curve two convoluted oxidation peaks are observed. One possible explanation of the presence of such two peaks can be attributed [11] to the formation of both a Mn^{III} oxide and another compound which could be K-birnessite, in which manganese has an intermediate oxidation state between three and four. The subsequent reduction presents a modified peak due to the decrease of the Mn^{IV} content in the oxide.

Though similar in the features of the curves, the various samples behave differently as for the quantity of charge passed during reduction and oxidation and for the cyclability. Table 1 reports the values of the specific capacity during reduction (Q_{red1} and Q_{red2}) and oxidation (Q_{ox1} and Q_{ox2}) at the first and second cycles. It can be easily seen that MNAL0 behaves better than the commercial samples (see also Fig. 3). The best result is, nonetheless, presented by MNAL5 (Fig. 4). Al shows an undoubted beneficial effect when present in a limited range of quantities only. Comparison of the results for MNAL05 and MNAL05B in Table 1 puts in evidence that the inversion in the addition of the reagents during preparation seems to enhance the performance of sample.

Analysis of the capacity data can give some information about the cyclability of the samples considered. The significance of these findings is of course limited as they regard two cycles only. Table 2 reports in its columns the ratio (in percent) between the charge passed during one branch of a cycle and that passed during the preceding branch

Table 2

Ratio (in %) between the charge passed during one branch of a cycle and that passed during the preceding branch

	$Q_{\text{ox1}}/Q_{\text{red1}}$	$Q_{\text{red2}}/Q_{\text{ox1}}$	$Q_{\text{ox2}}/Q_{\text{red2}}$
MNAL0	62	72	100
CMD	35	73	82
EMD	64	42	82
MNAL05	68	78	100
MNAL05B	100	63	100
MNAL5	62	75	84
MNAL10	77	70	100

cycle and that passed during the preceding branch: Q_{ox1}/Q_{red1} (first column), Q_{red2}/Q_{ox1} (second column) and Q_{ox2}/Q_{red2} (third column). The first column values show that only in the case of MNAL05 the charge passed during reduction is completely restored during the subsequent oxidation. This means a complete recharge of the discharge electrode. This good result is extended to the second cycle, third column, to almost all the laboratory prepared samples. This performance, that needs to be confirmed by repeated cycles, is therefore, more strictly related to the kind of preparation than to the presence of Al. The second column reports that for all the samples the charge passed during the second discharge (red2) is less than that acquired during the first recharge (ox1). This is an expected phenomenon, due to the fact that the structure of manganese dioxide restored during the first recharge is different from the original one.

3.3. Morphology examination

SEM examination of the samples revealed that the commercial samples differ from the laboratory prepared ones for

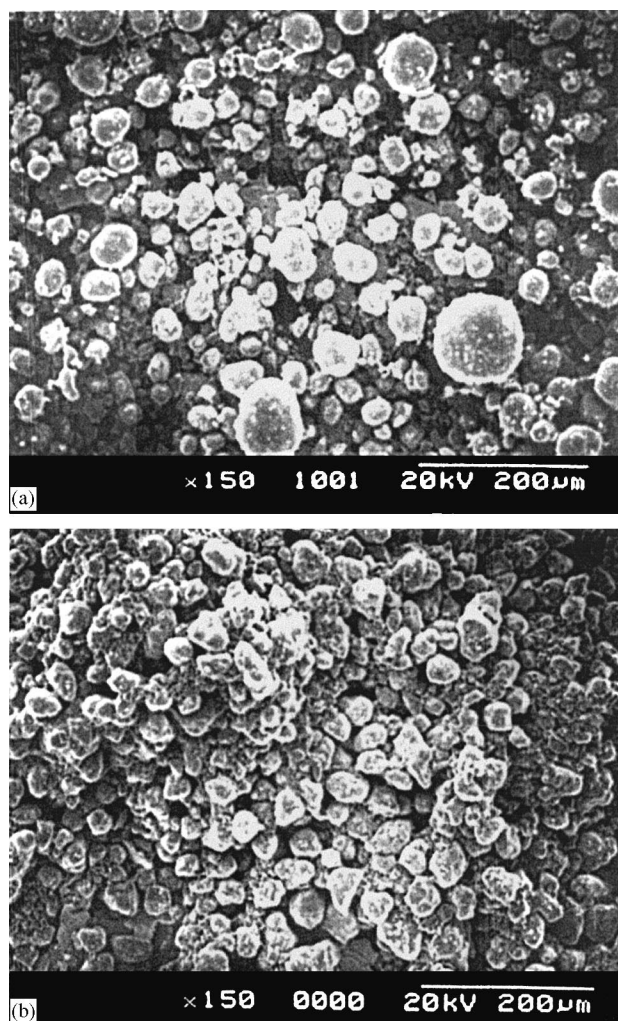


Fig. 5. SEM micrographs of CMD (a) and MNAL0 (b) samples. Magnification: 150 \times .

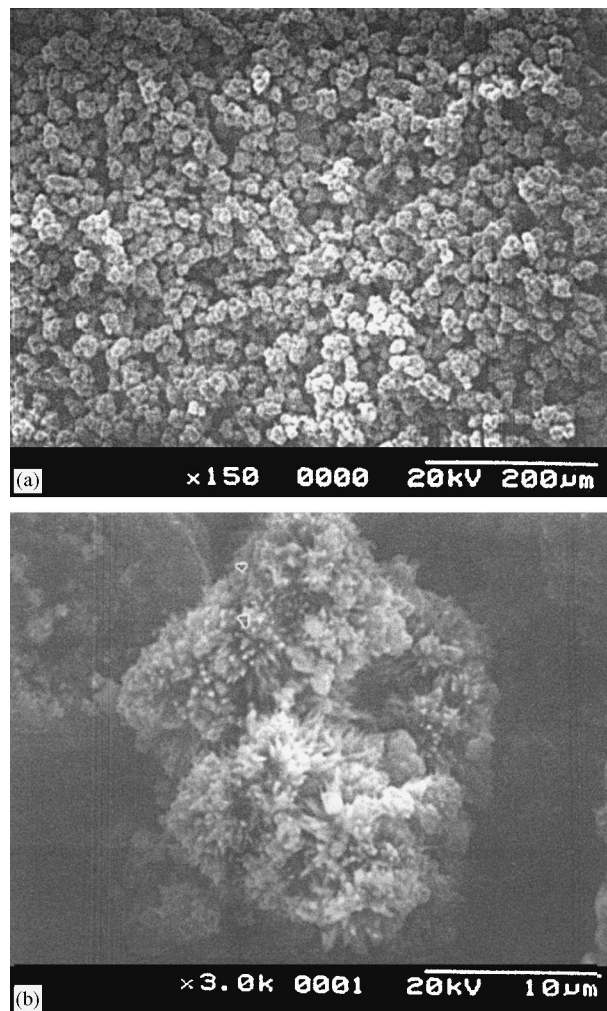


Fig. 6. SEM micrographs of MNAL5 sample. Magnification: 150 \times (a) and 3000 \times (b).

the grain size being for the lab prepared samples much lower and homogeneous in the dimension (Fig. 5a and b). In the case of Al containing manganese dioxides, the grain surface is not smooth but appears covered with needle like structures (Fig. 6a and b). Such feature appears particularly important from the conductance viewpoint as these needles should allow a much better connection of MnO_2 with graphite so at least in part explaining the higher currents shown in the electrochemical tests by these compounds.

4. Conclusions

Laboratory samples with different defectivities have been prepared by a modified chlorate method. Aluminium free manganese dioxide exhibits an EMD-like structure, it was found that the presence of Al modifies the structure by increasing the degree of disorder and by even making it similar to that of CMD.

The experimental results indicated a possible correlation between the structure and the electrochemical properties. In

fact, the samples, for which the splitting of lines h21/h40 in X-ray patterns is more evident (a typical feature of the orthorhombic CMD-like structure), present a similar trend of the voltammetric curves.

In agreement with literature data, the electrochemical reduction of the tested samples is affected by KOH concentration. In 1 M KOH a single reduction peak is found, related to the proton insertion step, while in 9 M solutions the reduction curve is the result of two reaction steps, which, in our experimental conditions, yield two non-distinguishable overlapping peaks.

In 1 M KOH solutions, aluminium containing compounds present an electrochemical activity similar to commercial oxides. The intriguing aspect is that the effect of aluminium is not directly relatable to the added quantity.

Our experimental data show that in 9 M KOH the pure laboratory sample and some Al containing MnO₂ powders show a higher discharging capacity and seem to assure a higher cyclability and an almost complete recharging from the second cycle on.

In 9 M KOH solutions, the highest electrochemical capacity is performed by the samples (MNAL0 and MNAL5) whose structures show a high degree of disorder in terms of defective situations of the lattice.

Finally, the high current shown during discharge by some of the Al containing samples can be related to some typical morphological features that seem to assure a better contact between graphite and MnO₂.

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