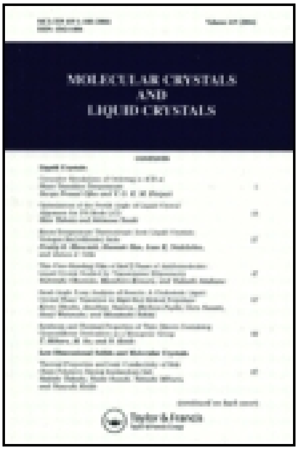

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Alkaline Battery Active Manganese Dioxides: Electrochemical Activity, Reversibility and Proton Diffusivity

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ALKALINE BATTERY ACTIVE MANGANESE DIOXIDES : ELECTROCHEMICAL ACTIVITY, REVERSIBILITY AND PROTON DIFFUSIVITY.

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Abstract

Chemical disorder of battery active manganese dioxides (MD) evidenced as Mn^{3+}, Mn vacancies and OH groups, is associated to well identified structural defects. Structural analysis of ordered-disordered MD with increasing defects content relates Mn^{3+} to inter growth defects (Pr) and Mn vacancies to micro twinning (Tw). Potentiostatic reduction studies in 1N KOH provide I(V) and V(x) curves which show a correlation between the potential of the maximum intensity of the reduction current, the chemical and associated structural defects and the reduction kinetics of respectively EMD, CMD and ramsdellite. Reversibility is obtained for the two first forms in oxidation.

Keywords: chemical-structural disorder, electrochemical reactivity, slow voltametry, proton diffusivity.

INTRODUCTION

Battery active manganese dioxides are disordered materials whose electrochemical activity is due to the presence of chemical and associated structural defects induced by the synthesis process. It mainly consists to oxidise by chemical or electrochemical way a Mn^{2+} salt to MnO_2 : the first step of the reaction corresponds to the oxidation of Mn^{2+} into Mn^{3+}. The manganese oxidation state III is unstable, Mn^{3+} disproportionates then into Mn^{2+} and Mn^{4+}: Mn^{2+} remains in solution whereas Mn^{4+} gives rise, at the potential value of water oxidation, to the solid MnO_2 deposit which trapped

Mn^{3+} traces. All these MD have in common a disordered structure associated to a non stoichiometric chemical formula defined by Ruetschi [1] as:

$$Mn^{4+}{}_{1-x-y}\,Mn^{3+}{}_{y}O^{2-}{}_{2-4x-y}\ V^{oooo}{}_{x}\ (OH)^{-}{}_{4x+y} \qquad (1)$$

in which Mn^{3+}, manganese vacancies V^{oooo} and associated OH are evidenced. It seemed interesting to look precisely at the influence of these defects on the MD electrochemical activity. Different methods were used: XRD to gain a precise structural characterisation of the defective MD, potentiostatic reduction by steps of 10mV each 2 hours to gain the capacity reduction rate with time.

The aim of this work is to correlate the chemical defects to the structural defects and their influence to the electrochemical activity during the reduction by proton insertion in 1N KOH on well characterised CMD/EMD and stoechiometric MD.

EXPERIMENTAL.

Materials

Several MnO_2 forms were examined : natural ramsdellite from New Mexico "NM R", synthetic ramsdellite "S-R" prepared by a modified hot acid treatment of $LiMn_2O_4$ [4], a commercial chemical manganese dioxide "WSA" from Sedema, as used in our previous studies [2-5], an EMD from DELTA (South Africa) and a series of EMD samples laboratory prepared at 97°C in a 0.5 M Mn^{II} sulphuric solution at pH1 with increasing current densities from 0.024 $A.dm^{-2}$ to 1 $A.dm^{-2}$ [6].

Methods

Physico-chemical Characterisation.

Each sample was characterised by X-ray diffraction (XRD), chemical and thermogravimetric analysis. XRD patterns were recorded on a Siemens D5000 diffractometer equipped with a diffracted-beam monochromator and Cu Kα radiation. XRD diagrams were analysed with the structural model proposed recently by Pannetier [2], which analyses the great variety of the powder patterns of battery-active manganese dioxides with two kinds of structural defects [2]: (i) de Wolff defects : the random inter growth of pyrolusite structural blocks in the initial ramsdellite network, (ii) micro twinning of the orthorhombic ramsdellite type lattice on the 021 and/or 061 planes.

Electrochemical methods

The electrochemical response of samples was analysed using a 'MacPile' computer-controlled system (Biologic, Claix, France). For an accurate determination of the I(V) and V(x) curves, composite positive electrodes made of 0.1g MnO_2 and graphite (1/3 in weight) were reduced in 1M KOH under potentiostatic control with a step scanning rate of 10 mV/2 hours. The experimental cell is described elsewhere [3].

RESULTS.

Structural characterisation.

The XRD pattern evolution of laboratory prepared EMD, given on Figure 3 evidences the shift of several diffraction lines leading to the decrease of their number when the deposition current density increases. Their analysis using the structural model developed in ref [2] shows an evolution from pseudo-orthorhombic to hexagonal system in which the Pr (De Wolff defect rate) does not vary whereas Tw the micro twinning rate increases with current density [2,6]. Physico chemical analysis reveals a simultaneous density and Mn percentage decrease in MD formula when the current density increases [6]. The constancy of Pr in these samples prepared from electrolytic solutions having the same conditions of pH, temperature and Mn^{II} concentration leads to relate inter growth defects to the presence of Mn^{3+} traces and micro twinning to manganese vacancies created by oxygen evolution, concomitant to MnO_2 deposit.

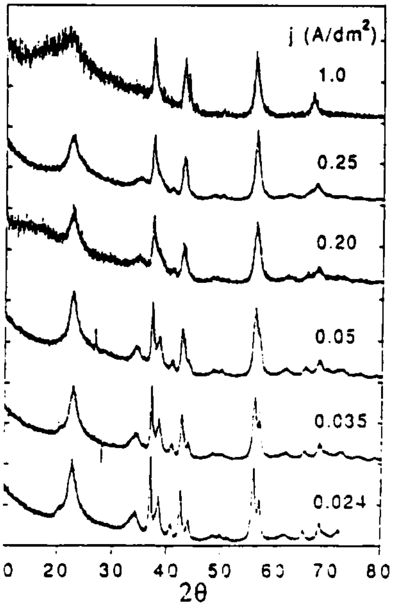

FIGURE 1 X-rays diagrams of EMD deposited in 1N SO_4H_2 and 0.5M Mn^{II} at 97°C, with increasing current densities from 0.024 to 1 A./dm^2.

Table I gives the cristallochemical characteristics of the samples under study : natural and synthetic ramsdellite, groutellite, CMD WSA, IBA11 and EMDs, in terms of Mn/O ratio, Pr and Tw.

TABLE I Chemical and structural characteristics of natural and synthetic MD.

sample	Mn/O	Pr	Tw (%)
pyrolusite (β-MnO_2)	2	1	0
ramsdellite	2	0	0
groutellite $MnOOH_{0.5}$	2	0	0
Synthetic ramsdellite	1.98±0.02	0.2	20
CMD WSA	1.97±0.02	0.45	35
EMD DELTA	1.95±0.02	0.45	100

Electrochemical measurements

Comparison of CMD-EMD I(V) and V(x) curves recorded during the reduction by 10mV/2hours steps in 1N KOH (Figure 4) with the ones of the ordered and stoichiometric forms leads to the following observations: at -0.1V (ref Hg/HgO KOH 1N) NM-R is not yet reduced, 15% of S-R capacity, 35% and

55% of the one of respectively CMD WSA and EMD is recovered . Synthetic ramsdellite has an intermediate reactivity between CMD and ramsdellite : its capacity is mainly recovered below -0.1V and shared between two sites of -0.1V and -0.3V respectively [4]. From the comparison of CMD WSA and EMD Delta reduction voltamogram, the presence of higher Tw rate in EMD allows to recover faster a greater capacity than from CMD.

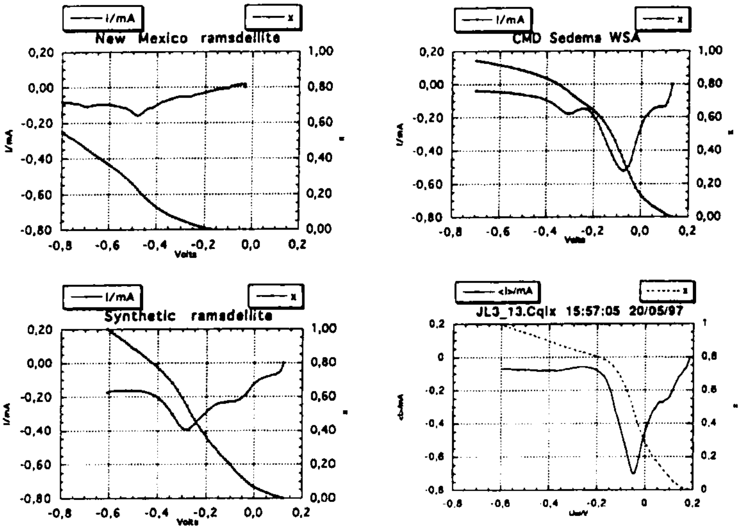

FIGURE 4 Potentiostatic reduction of the R, sR, CMD and EMD with a scan rate of 10mV/2h in 1N KOH. The full line represents the variation of incremental capacity $\delta x/\Delta V$ with potential V, the dotted line the variation of reduction rate x with potential.

It appeared interesting to study by EIS the proton insertion kinetics and determine the proton diffusion coefficient in both materials during the potentiostatic reduction, in order to check the influence of the structural/chemical disorder on the geometry and on the value of the diffusion motion [7,8]. The results of the Electrochemical Impedance Spectroscopy study will be published elsewhere [9].

DISCUSSION-CONCLUSION.

Careful characterisation of ordered and disordered MD leads to their classification among increasing Pr and Tw defects rate. Their potentiostatic reduction in 1N KOH under the same voltage scan rate provides a reactivity scale which parallels the one of structural defects rate.

From the data given on Table I , one can observe Pr goes from 0 (R), 0.2 (S-R) to 0.45 (CMD /EMD), Tw from 0 (R), 20% (S-R), 35% (CMD) to 100% (EMD). Comparison of CMD-EMD reduction voltamogrames by 10mV/2hours steps in 1N KOH (Figure 3) with the ones of the ordered and stoichiometric forms leads to the following observations : R does not deliver any capacity at -0.1V (ref Hg-HgO), S-R, CMD WSA and EMD respectively 18%, 35% and 55% of their capacity at -0.1V. S-R has an intermediate reactivity between CMD and R : its capacity is shared between two sites of -0.3V and -0.1V respectively, whereas R deliveres a small part of its capacity at -0.4V and CMD the main part at -0.1V. The presence of mainly Mn^{3+} defects (Pr=0.45) in CMD WSA appears to increase the reduction peak potential to -0.1V compared to NM-R and S-R, whereas the Tw=100% in EMD associated to Mn vacancies increases this potential to -0.05V and makes the reduction kinetics faster (55% of EMD capacity recovered at -0.1V, compared to the 35% of CMD). These results show more precisely how structural and chemical disorder develops the electrochemical activity of MD in 1N KOH in increasing simultaneously the potential and the kinetics of reduction by proton-electron insertion [4]. In reference to an electronic band model, the occurrence of Mn^{3+} defects fills the gap with free electrons and Mn vacancies create holes in the valence band : both increase the Fermi level energy of these disordered MD, consequently their electrode potential.

The evaluation of the possibilities of EIS to check not only the reduction kinetics but also the geometry of the diffusion [10] during the reduction by proton/electron insertion in 1M KOH of the two well characterised CMD and EMD samples is presently under study.

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