MANGANESE DIOXIDES FOR ELECTROCHEMICAL STORAGE OF ENERGY

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Introduction

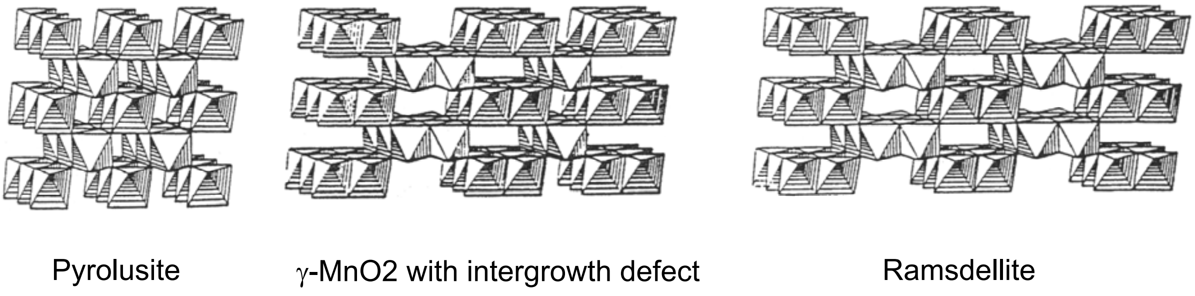
MnO_2 (MD) exist under numerous natural (pyrolusite, ramsdellite, nsutite, birnéssite, todorokite, psilomelane) and synthetic (a, b, g/e, d, !) forms. After a brief review of the natural forms, the synthetic ones are examined in view of their applications for electrochemical energy storage. A particular attention is devoted to the synthetic and disordered g/e forms active in alkaline batteries, to illustrate the great sensitivity of MnOx to synthesis conditions.

Experimental

The most active γ/ε MD are mainly prepared by electrodeposition (EMD) from a hot and acidic solution of MnSO4 (95°C, pH 1). Mn^{2+} is oxidised into Mn^{3+} unstable in acidic medium it disproportionate to Mn^{4+} which generates anodic deposits of MnO_2 simultaneously with oxygen evolution. Both reactions generate chemical defects responsible for MD's structural disorder illustrated in the Rütschi [1] formula:

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

and responsible for their electrochemical activity.



Pyrolusite γ-MnO2 with intergrowth defect Ramsdellite

***Fig. 1** A polyhedral representation of the close-packed structure of pyrolusite or β-MnO_2 , ramsdellite, and γ-MnO_2, on which the intergrowth of a pyrolusite structural block in the ramsdellite lattice represents the De Wolff defects.*

Results and discussion

A structural model was proposed to analyse the XRD pattern [2], based on two types of defects: intergrowth of tetragonal pyrolusite structural blocks in the orthorhombic ramsdellite network (the De Wolff disorder [3]), and microtwinning of this interspersed structure. Pyrolusite-type defects in a ramsdellite structure can be expressed quantitatively using Pr, defined as the probability that the 'next' neighbour is pyrolusite-type. Hence Pr = 0 for ramsdellite, Pr = 1 for β-MnO_2 (pyrolusite) and $0 < Pr < 1$ for the γ-MnO_2 series. Twinning (Tw) of the orthorhombic ramsdellite lattice was necessary to explain the reduction to 6 broad lines in the XRD pattern for some EMD (presented on Fig. 3 in [5]) as well as the occurrence of an apparently hexagonal structure. Both parameters Pr and Tw are calculated from the analysis of diffraction patterns among the protocol defined in [4]. Ranking of γ/ε-MD in terms of increasing Pr and Tw defects parallels that of electrochemical activity [6-10]. These structural parameters are related to chemical disorder [8]: Pr is induced by the presence of Mn^{3+} and Tw is associated to the occurrence of manganese vacancies ($V^{\circ\circ\circ\circ}$). They are shown to govern structural [8], electrochemical [9] and surface properties [11-13] of γ-MnO_2

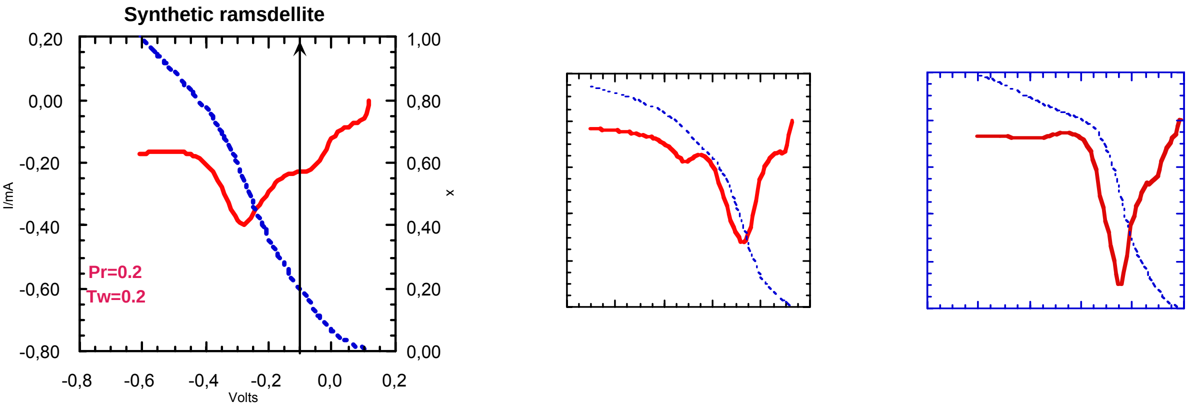


Fig. 2 *Influence of Pr rand Tw on the electrochemical spectra of g-MnO2 [6].*

Potentiostatic reduction curves recorded with a 10 mV/2h scan rate of g-$MnO_2$are presented in Fig.2.: Increasing percentage of defects quantified by Pr and Tw improves g-MD electrochemical activity. For Pr=0 (ramsdellite) and Pr=1 [fig.3 micro-ḅ I(V) curve], the reduction potential is low (-0.5V vs Hg-HgO). For g-MD with larger Pr rand Tw, reduction potential is increased to : Pr=0,2 and Tw=0,2 (Isynthetic ramsdellite) the capacity is recovered at -0.35 V (ref Hg-HgO), at -0.1 V for CMD Sedema WSA with Pr=0.45 Tw=0.36. For similar Pr, high Tw value increases both reduction potential and kinetics (EMD Delta).

If Turner and Busek provided HRTEM images illustrating the intergrowth defects in 1983 [14]. Heuer et *al* looking recently for HRTEM image of the “twinning defect” only evidenced “structured” nano-aggregates which were confirmed to represent microtwinning: figure 3 shows the increase in potential carried out by the nanometric dimension during the reduction of a nanocrystalline β-MnO_2 [16].

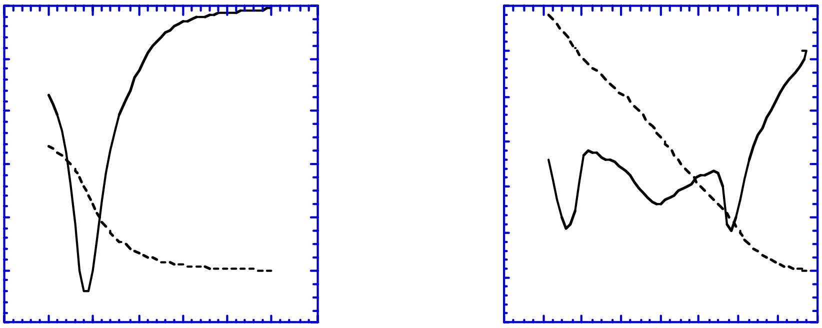


***Fig. 3** I (V, x) Potentiostatic Reduction curves (scan rate 10 mV/2h): micro-β (left) and nano-β (right) in 1M KOH (reference electrode Hg-HgO). Continuous line: (I, V), dotted line: (x, V) curves. X, the reduction rate at –0.6V, is 1 for nano- β (x=1), low for micro-β (x=0.3).*

Conclusions

Electrochemical activity of geMnO$_2$ is shown to be mainly controlled by chemical and associated structural defects quantified with the structural parameters Pr and Tw. Relationships are evidenced between Pr – Tw and the main electro-deposition parameters (bath temperature, concentration in MnSO4, pH, current density) which allow to prepare EMD with required activity. Doping EMD with Ti or Fe amplifies the heterogeneous reduction mechanism in 9M KOH. Depending on the type of reduction process required (fast reversible discharge, or deep discharge) it is possible to obtain g-MnO$_2$ of precise activity.

Except the stable phases b-MnO$_2$, Mn$_2$O$_3$ and Mn$_3$O$_4$, manganese oxides exist over a very large number of isotypes, very sensitive to synthesis conditions. They are well documented over the last decades for lithium insertion, a lot remains to be done for MnOx phases devoted to supercapacitors and AFC cathode catalysts.

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