ORIGINAL PAPER

Preparation and properties of manganese dioxide studied by QCM
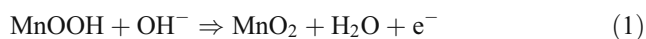
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Abstract Electrodeposition and cycling of MnO_2 was tested by cyclic voltammetry and electrochemical quartz crystal microbalance (QCM). The electrodeposition from manganese sulfate and the material cycling are accompanied by strong and almost reversible water sorption close to the stoichiometric ratio 3:1. Similar reversible sorption of water was observed also on solid MnO_2 deposited as an "ink" (slurry) with polytetrafluoroethylene as a binder on the QCM probe.

Introduction

Manganese dioxide is an active material widely used in batteries as the positive electrode. It has been carefully investigated more than 80 years. Despite this, there still seems to be more to investigate concerning the generation and phase transformations (aging) during the process of cycling [1–4]. The only type of manganese dioxide used in commercial cells is the electrolytic manganese dioxide (EMD; γ-MnO_2). The electrochemical redox reaction of this secondary cell system is commonly formulated according to the scheme [5–7]:

$$MnOOH + OH^- \Rightarrow MnO_2 + H_2O + e^- \qquad (1)$$

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The mechanism is very complex, but we are still in progress on understanding all the electrochemical aspects. Their structure in general consists of octahedrons MnO_6. Plenty of substoichiometric forms are known and a formula such as the substoichiometric phase MnO_{2-x} would be appropriate for them. This material can be prepared either by reduction of permanganate or oxidation of manganese salts. Both methods can be performed electrochemically.

Numerous papers were devoted to the electrochemistry of manganese oxide in relation to its application in batteries. All forms prepared at low temperatures contain a rather high amount of water. Therefore, the uptake and/or removal of water in the course of their formation or cycling in a battery is rather important. This aspect became apparent in the last decade.

The amount of residual water content is known to be important for the performance of MnO_2 in aqueous batteries as well as nonaqueous ones (for example, [8, 9]). Another example is that the complete removal of water from γ phase may result into its change to β phase, which is not applicable as cathode material for lithium-ion batteries. Therefore, the study of water residuum is rather important both from scientific and application viewpoints.

The use of electrochemical quartz crystal microbalance (QCM) can help to clarify the mass changes during cycling (charging and discharging) and to determine the nature of involved species.

Few papers have been devoted to the use of QCM for the investigation of electrodeposited MnO_2. For example, Bach et al. [10] studied the intercalation of lithium into layered manganese/lithium compounds. Devaraj and Munichandraiah [11] investigated the electrodeposition of MnO_2 for the use as electrodes in electrochemical supercapacitors, and Owen et al. [12] investigated the nucleation of MnOOH from manganous salts with Mn^{3+} entities as intermediates.

An extensive study was presented by Uchiyama et al. [13]; this paper describes the nature of the manganese oxide deposited from different solutions. The importance of water absorbed simultaneously to the charging and discharging process and the deactivation of the electrode due to the material dissolution in subsequent cycles were studied at first by Wu et al. [1]. Properties of MnO_2 films prepared by ways different from electrolytic oxidation of manganous salts are not considered in present paper.

The operation of the QCM is based on the use of quartz resonators in the form of a thin quartz crystal, which has thin metal film electrodes on its both sides. The electrodes are used to generate the oscillation in the quartz crystal, and the frequency change is the measure of mass changes of the material deposited on the working surface [14]. Mass changes accompanying electrode processes can be observed in this way. For thin rigid deposits, the change in the resonant frequency of the oscillating crystal (Δf) is proportional to the change in mass (Δm) per unit area (A) of the deposit on the working electrode as described by the Sauerbrey equation:

$$\Delta f = -\frac{2 \times \Delta m \times f_0^2}{A \times (\mu \times \rho)^{1/2}} \quad (2)$$

where f_0 is the fundamental frequency of the crystal and μ is the shear modulus (2.95×10^{11} g cm^{-1} s^{-2}) and ρ is the density of quartz (2.65 g cm^{-3}).

The resonant frequency is directly connected to mass changes on the surface of the crystal. The other option is the observation of damping. It is based either on the width of the resonance line or by other electrotechnical means, and it results in the description of the rigidity, viscosity, or other parameters of the surface layer on the crystal. This option was not used in the research described in here. Only gravimetric mode was used and evaluated.

The electrodeposited oxide was compared to commercial manganese dioxide deposited by our procedure on the QCM crystal. Substance known as γ-MnO_2 is most often prepared by electrodeposition onto an anode from an electrolytic solution of $MnSO_4$, and some sulfuric acid can be added into the solution to improve the deposition [9, 14] according to an equation

$$Mn^{2+} + 2H_2O \Rightarrow \gamma MnO_2 + 4H^+ + 2e^- \quad (3)$$
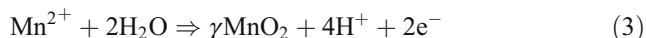
followed by washing and drying. The γ MnO_2 prepared in such a way is called EMD [15, 16].

Cartwright and Paul [17, 18] have used a variety of techniques for the study of this process. They formulated two possible electrodeposition mechanisms, i.e., mechanism A consisting of two one-electron steps (in brevity, $Mn^{II} \rightarrow Mn^{III} \rightarrow Mn^{IV}$) and mechanism B based on a direct two-electron oxidation ($Mn^{II} \rightarrow Mn^{IV}$).

The behavior of commercial EMD is somewhat simpler. Its tunnel-like structure can accommodate fairly easy smaller cations such as hydroxonium, lithium, or sodium. Also this process is fairly reversible and used in batteries and electrochromic devices nowadays.

After we governed the QCM technique, we decided to investigate several electrochemical processes by it. The main goal of this paper was to show the importance and reversibility of water incorporated into the Mn oxide simultaneously with its growth and during the cycling of manganese dioxide in the form of thin layers.

Experimental

The QCM device QCM200 (product of SRS) was used for both sample deposition and investigation together with potentiostat PGSTAT 12, EcoChemie, The Netherlands. The output plotted as mass changes against potential is called "massogram" in this paper.

The exposed area of the active electrode (platinum) in contact with the electrolyte is 1.37 cm^2 (the displacement area between the two circular electrodes is 0.4 cm^2). The resonant frequency of crystal is 5 MHz, and its sensitivity factor C_f is 56.6 Hz μg^{-1} cm^2.

The crystal was calibrated by electrodeposition of copper by a known amount of charge passed in a galvanostatic mode. The calibration constant corresponded roughly to that evaluated by generally known Sauerbrey equation.

The samples were prepared by electrodeposition from a 0.1-M solution of $MnSO_4$ in distilled water.

For comparison, also solid manganese dioxide MnO_2 (EMD, Knapsack, battery grade) was investigated under the same method and condition. The powder (0.01 to 0.05 mm in diameter) was mixed with water and isopropyl alcohol to which small quantity of polytetrafluoroethylene suspension (3% to 4% by wt.) was added and dispersed by sonication. Small amount of this "ink" was deposited on the crystal (located horizontally) either by spraying or by a brush and dried.
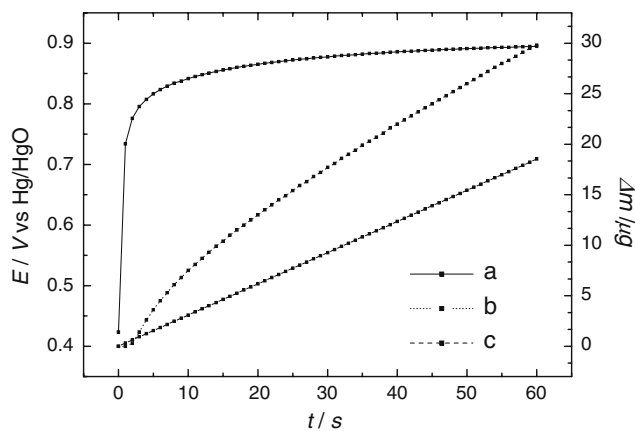
The investigation itself proceeded in 1 M KOH deaerated by nitrogen. Potentials are related to a Hg/HgO/1 M KOH reference electrode.

Results

Electrodeposited MnO_2

Deposition of MnO_2 layers

An example of manganese oxide electrodeposition is plotted in Fig. 1. The deposition current density was
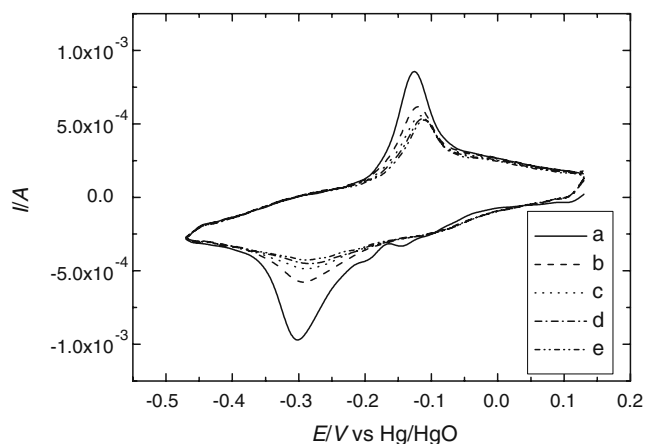
Fig. 1 MnO$_2$ electrodeposition, potential E/V (*full line*), calculated by Faradays law (*punctuated line*) and measured by EQCM (*broken line*) mass dependence

Fig. 3 Cyclic voltammetry and massogram comparison of electrodeposited MnO$_2$ in 1 M KOH, scan rate 10 mV/s, N$_2$ bubbled, *a* CV (*left scale*, current) and **b** mass change (*right scale*)

0.5 mA cm^{-2}. At the end, the charge passed corresponded to 18.5 μg of deposited layer MnO$_2$. On the contrary, the mass increase about 29.8 μg was estimated from the output of the EQCM device, which is by 11.3 μg more. The simultaneous incorporation of water seems to be evidenced by our experiments. The molar ratio between water and MnO$_2$ is then 2.95:1 approximately.
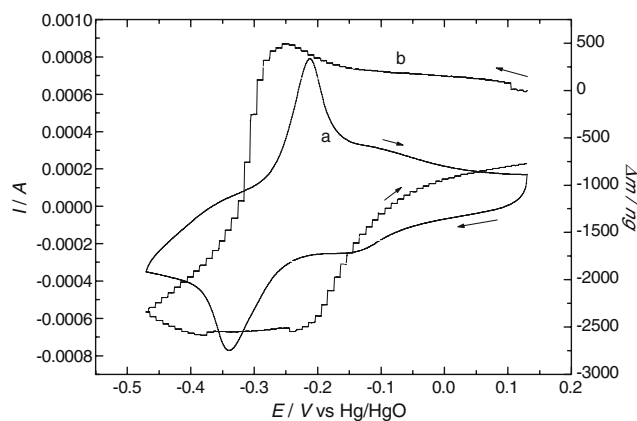
Voltammetry

Charging and discharging of MnO$_2$ was tested by cyclic voltammetry (scan rate 0.01 V s^{-1} was used). A cathodic process at −0.3 V (vs. Hg/HgO electrode) and its opposite process at −0.125 V (see Fig. 2) were observed on voltammograms. Their magnitude decrease in subsequent cycles is clearly indicated there.

The behavior of another electrode in 1 M KOH (scan rate 10 mV/s, N$_2$ bubbled) is shown in Fig. 3. This
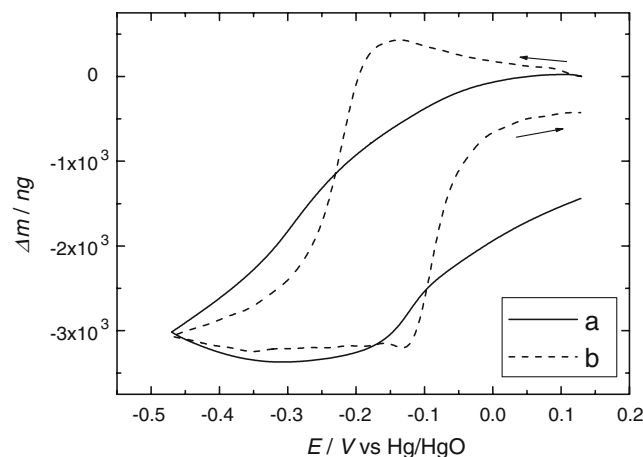
voltammogram was recorded on the second scan; the first scan is not plotted there.

We can see distinct mass changes in the potential range of both anodic and cathodic voltammetric peaks. Apparently, the reduction is accompanied by mass loss, and the oxidation (i.e., charging) is bound to mass increase.

The comparison of mass computed from the charge passed through the system and the output of the EQCM are compared in Fig. 4 by integration of voltammograms.

The mass from the charge is compared under the assumption of one molecule of water per one atom of Mn^{4+} changed to Mn^{3+}. Again we can see that the material releases water in the process of reduction in an amount higher than one molecule to one atom of manganese.

It should be noted that the massogram (the Δm vs. potential) is not closed. This indicates that the sorption and desorption of water is not quite reversible, and some water remains in the substance. Hence, the uptake of water is bound to the oxidation/reduction process indirectly only.

Fig. 2 Cyclic voltammetry, electrodeposited MnO$_2$ in 1 M KOH, scan rate 10 mV/s, N$_2$ bubbled. From *top* to *down*: scan 1 (*a*) to scan 5 (*e*; on anodic runs)

Fig. 4 The integral of current (*full line*) and measured mass changes (*broken line*) mass flow in electrodeposited MnO$_2$ in 1 M KOH, scan rate 10 mV/s, N$_2$ bubbled, scan no. 2
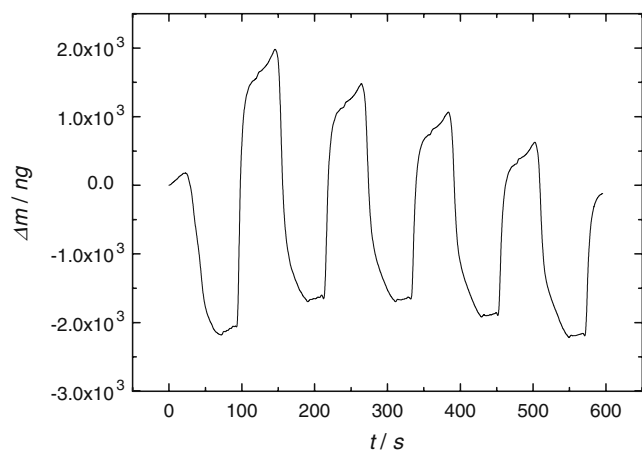
Fig. 5 Time dependence of mass flux of MnO_2 in 1 M KOH, scan rate 10 mV/s, N_2 bubbled, first five scans

Apparently, some water remains after the cycle had finished.

Finally, the influence of cycling on the process is shown in Fig. 5 in the course of five discharging cycles.

We can see a steady decrease both of the depth of the changes in one cycle and the total mass of the electrode, which indicates the termination of the life of the system perhaps due to slow dissolution of manganese oxide layer in the electrolyte or by swelling of the material by the insertion of water molecules.

Solid MnO_2 deposited in an "ink"

The QCM sensor electrodes covered by slurry of solid oxide were investigated by voltammetry using scan rate from 50 to 0.2 mV/s. An example of a voltammogram is given in Fig. 6, while the massogram and the mass estimated from the charge (integral) of voltammetric curve is demonstrated in Fig. 7. Various values of apparent mass of substance absorbed or released by the electrode were
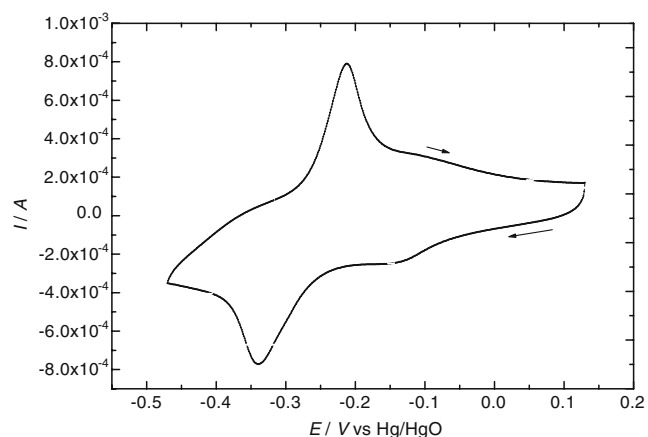
Fig. 6 Example of a voltammogram of a MnO_2 electrode (solid commercial oxide deposited as an ink) at scanning rate 0.01 V s^{-1}
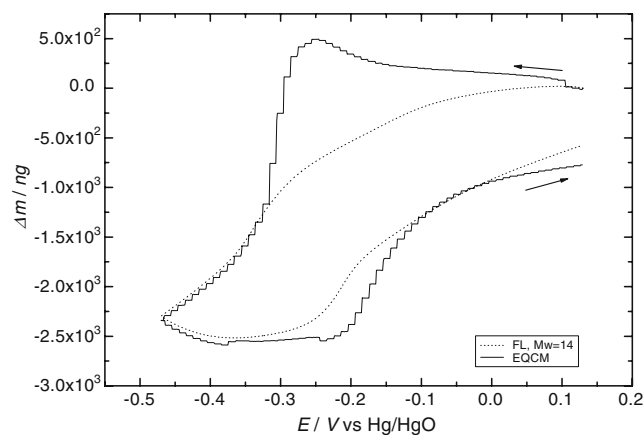
Fig. 7 Mass change (output from QCM, *solid curve*) compared to integrated voltammogram (*broken line*) computed using apparent molecular weight equal to 14 U. Experiment the same as in Fig. 6

used so that both curves coincided reasonably. The values of apparent mass were dependent on scan rate, as it is indicated in Table 1.

Discussion

The values of apparent molecular weight (see Table 1) do not correspond to a clear stoichiometric ratio. However, they cannot be neglected for the explanation of cycling and lifetime of MnO_2 electrodes in electrochemical power sources.

The formation of MnO_2 by electrochemical deposition corresponds to the ratio two or one atoms Mn to two to three molecules of H_2O. We suppose that this water is incorporated in the tunnels existing in the structure of the oxide.

More difficult for explanation are the mass changes accompanying "charging" and "discharging" (i.e., oxidation or reduction) of the oxide. The usual explanation of the electrochemical process is based on formation of oxide–hydroxide MnOOH from the dioxide. Such a reaction is not accompanied by any massive mass change. Another possibility would be the hydration of the electrode and reaction chain incorporating entities $Mn(OH)_xO_y$, for example, $Mn(OH)_3$ and $Mn(OH)_4$. However, no other experimental evidence is known at this moment, and it does not seem to be the most probable one. Such a process

Table 1 Apparent molecular weight m_{app} at various scan rates v (millivolts per second)

The apparent molecular weight m_{app} obtained from comparison of massograms and charge (integrated current) on voltammetric curves

Scan rate v	m_{app}
50	9
25	14
10	18
1	30
0.5	6

is expected in electrodes $Ni(OH)_2$; the α-form accepts one hydroxyl, while the β-form gets rid of one hydrogen atom and their transformation can be monitored by QCM quite clearly from our unpublished results.

Undoubtedly, the incorporation and expelling of water changes the state of hydration of the material as well as the dimensions of elementary lattice. These processes are undoubtedly one of the reasons for shortening lifetime and cycle life of MnO_2 electrodes in power sources.

Also a mechanism involving the insertion of a hydronium ion H_3O^+ is considered for the reduction of metal oxides in acidic medium; the formation of "tungsten blue" from WO_3 is often discussed and verified by QCM. However, it does not seem quite probable for the processes in alkaline media.

From the different shape of massograms and charge (for example, see Fig. 3 or Fig. 4), we can come to the opinion that the uptake and release of water proceeds more slowly than the electrochemical oxidation–reduction itself. It follows from the marked peak on massogram, which is absent on the mass derived from the charge (Figs. 4 and 7). This peak is apparent in the potential range in which the greatest transfer of charge occurs, and therefore, we can conclude that it is due to the electrochemical insertion reaction. However, the uptake of water is also controlled by the potential and/or oxidation state, and some effect is to be ascribed to solvation of manganese oxides formed and decomposed during the cycling. This other process seems to be slower than the other one, but the influence of the first one does seem to be indicated clearly.

The cycling is almost reversible (see Fig. 5). However, a slow decrease of electrode mass confirms the theory of slow corrosion or dissolution of the oxide in the course of cycling. The best overlapping of mass evaluated from QCM output and obtained from integrated current was obtained assuming molecular mass of inserted substance equal to 14 approximately. Finally, it is interesting that the properties of commercial oxide (see Figs. 6 and 7) do not differ qualitatively from those of electrodeposited oxide.

Conclusion

It should be stated that the incorporation of water into the manganese oxide (presumably γ-MnO_2) plays an important role. The high ratio between the amount of water and oxidized atoms may be due to the structural features of the oxide, which is expected to contain a lot of structural voids and channels of a rather large cross section equal to two elementary octahedrons MnO_6. The occupation of them by water and/or by their hydration can depend on the degree of saturation. We explain in this way that there is no direct connection between accepted (or released) water and state of charge (oxidation level) and that both processes occur simultaneously and only indirectly coupled.

References

1. Wu BL, Lincot D, Vedel J, Yu LT (1997) J Electroanal Chem 420:159–161
2. Messaoudi B, Joiret S, Keddam M, Takenouti H (2001) Electrochim Acta 46:2487–2498
3. Nakayama M, Matsushima C, Ogura K (2002) J Electroanal Chem 536:47–53
4. Kirk RC, Fry AB (1948) J Electrochem Soc 94:277–281
5. Klápště B, Vondrák J, Velická J (2002) Electrochim Acta 47:2365–2369
6. Bezdička P, Grygar T, Klápšťě B, Vondrák J (1999) Electrochim Acta 45:6913–6920
7. De Wolff PM (1959) Acta Cryst 12:341–345
8. Devaraj S, Munichandraiah N (2009) Electrochem Solid State Lett 12:F21–F25
9. Jarvis L (1990) J Power Sources 32:271–276
10. Bach S, Pereiraraamos JP, Cachet C et al (1995) Electrochim Acta 40:785–789
11. Devaraj S, Munichandraiah N et al (2008) J Phys Chem C 112:4406–4417
12. Owen MP, Lawrance GA, Donne SW (2007) Electrochim Acta 12:4630–4639
13. Uchiyama T, Nishizawa M, Itoh T et al (2000) Proc Electrochem Soc Series 99:160–173
14. Buttry DA, Ward MD (1992) Chem Rev 92:1355–1379
15. Clarke CJ, Browning GJ, Donne SW (2006) Electrochim Acta 51:5773
16. Ward CB, Walker AI, Taylor AR (1992) Prog Batteries Battery Mater 11:40
17. Cartwright A, Paul RL (1980) In: Schumm B, Joseph HM, Kozawa A (eds) Proceedings of the MnO_2 Symposium, 2, pp 290
18. Paul RL, Cartwright A (1986) J Electroanal Chem 201:113–122