TRANSFORMATIONS OF MANGANESE OXIDES UNDER DIFFERENT THERMAL CONDITIONS

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Abstract

Thermal decomposition of various synthetic manganese oxides (MnO, Mn_3O_4, Mn_2O_3, MnOOH) and a natural manganese dioxide (MnO_2) from Gabon was studied with the help of termogravimetry in inert, oxidizing and reducing atmospheres. The compounds were characterized by XRD and electrochemical activity was tested by cyclic voltammetry using a carbon paste electrode. The natural manganese dioxide showed the best oxidizing and reducing capacity, confirmed by the lower temperatures of the transitions, the extent of the reactions and electrochemical performance in cyclic voltammograms.

Introduction

To understand the chemistry of manganese oxides it is important to know their crystalline structure. Thermal decomposition of the manganese oxides has been subject of many investigations by different authors [1–4]. These papers are related to the characterization and identification of polymorphic forms of manganese dioxide with the aim of selecting the more adequate MnO_2 for electrochemical applications. Natural manganese dioxide (NMD) is generally a mixture of different oxides and it could be applied as cathode material in primary cells.

The basic problem for NMD use is connected with its polymorphic form, its stability and transformation at different temperatures. The combination of thermal analysis and electrochemical measurements have several advantages to determine structural changes.

A few preliminary experiments were carried out to observe some electrochemical behaviour of manganese dioxides including NMD in alkaline electrolyte [5]. The use of carbon paste electrode has been converted into a

quick and non-expensive tool for morphological study of powdered solid compounds [6]. A simple cyclic voltammetry technique was used for evaluation of NMD as candidate for its use for cathodes of alkaline batteries. This method gives significant qualitative and semi-quantitative information. The proton transport along manganese dioxide structure in MnO_2 crystals is the most important kinetic step of discharge reaction at cathodes in alkaline cells [7]. The effect of these NMD solid-state properties were studied in relation to thermal behaviour and electrochemical one.

This paper summarizes analysis carried out on MnO, Mn_3O_4, Mn_2O_3 and MnOOH samples to compare with thermogravimetric behaviour of a NMD sample from Gabon. The crystalline structure of these compounds was analyzed by X-ray diffraction and confirmed with XRD patterns. A comparative discussion is presented about manganese compounds above mentioned during their thermal treatment in inert, oxidizing and reducing atmospheres. The thermal behaviour of natural manganese dioxide and its availability in primary cells, has been corroborated with results obtained by voltammetry at carbon paste electrode with KOH as electrolytic binder.

Experimental

Synthesis

The preparation of the different manganese oxides have been carried out by procedures described early. However, for the sake of ready reference, the methods of preparation are briefly summarized here:

- MnO: was prepared by starting with recrystallized manganous nitrate [8].
- Mn_3O_4: was prepared by thermal decomposition of manganous sulfate in air at 1000°C [8].
- Mn_2O_3 : since pyrolusite prepared by ignition of the nitrate, and converted this to partridgeite by ignition in air at 600°C [8].
- MnOOH: was prepared by precipitation of a manganous salt with ammonia in the presence of hydrogen peroxide [9].

X-ray diffractometry

XRD powder diffractograms were recorded step-wise (5°, 60 s) at room temperature, with a Philips PW 1710 diffractometer equipped with a copper anode generating CuK_α radiation ($\lambda = 1.5417$Å), in the 2θ range between 2 and 70°.

Thermal analysis

Thermogravimetric analysis (TG) was carried out using a Perkin-Elmer thermobalance TGS-2, using a linear heating rate of 20°C min^{-1} from 50 to 900°C,

and a gas flow of 30 cm^3 min^{-1}. In the reducing atmosphere, a mixture 1:3 hydrogen in nitrogen was used, maintaining the total flow pointed out before. All the gases were of a purity of 99.998%.

Cyclic voltammetry

The voltammograms were obtained with an Amel 553 potenciostat/galvanostat analyzer, coupled with an Amel 568 programmable function generator and an ADOSSIS® data acquisition program. An Ag/AgCl reference electrode was used with a platinum counter electrode. The working electrode was a carbon paste one with the solid electroactive substance incorporated [5]. Electrolyte density was determined by a densimeter Anton Paar model DMA-58 (±0.00001).

The voltammetric study was done in alkaline solution (KOH 8.5 M). Afterwards oxygen-free nitrogen was bubbled through the solution for ten minutes to deareate it. The stirring was stopped and a cathodic-anodic scan was carried out from zero current potential to −1.2 V, from this to 0.5 V and go back to the initial potential. The cyclic voltammograms were carried out at a scanning rate of 0.25 mV s^{-1} and at room temperature.

Results and discussion

In a complex system such as manganese oxides, difficulties in morphological studies arise from interpretation of data. XRD diffractograms were recorded to identify the resultant phases, because of the composition and structure of synthetic MnO$_x$ are largely dependent of the preparation variables. An automatic JCPDS library search was used for this purpose. In Table 1 are listed main structural data obtained from XRD analysis and the corresponding card of each synthesized oxide.

Stability and thermal transformations of the synthesized oxides have been studied by TG in inert, oxidant and reducing atmospheres. In Fig. 1 are plotted TG curves in nitrogen atmosphere for the studied compounds. It can be observed that MnO, Mn$_3$O$_4$ and Mn$_2$O$_3$ maintained stable at the studied temperature range. The synthesized MnOOH shows a first weight loss, close to 300°C, in which manganite is transformed to Mn$_5$O$_8$ and Mn$_2$O$_3$. In the second observed peak, the resultant compound is Mn$_2$O$_3$. Morgan et al. [10] reports another transition at 800–900°C in which the final compound is the Mn$_3$O$_4$. In our experimental conditions, this transition has not been observed. For the natural manganese dioxide, MnO$_2$, a progressive weight loss is observed from 200 to 580°C. That change is due to chemisorbed water loss and in this initial period, some O$_2$ is liberated too. At the end of this stage, an important weight loss 7.2%, takes place due to the transition from MnO$_2$ to Mn$_2$O$_3$ and it occurs at 620°C.
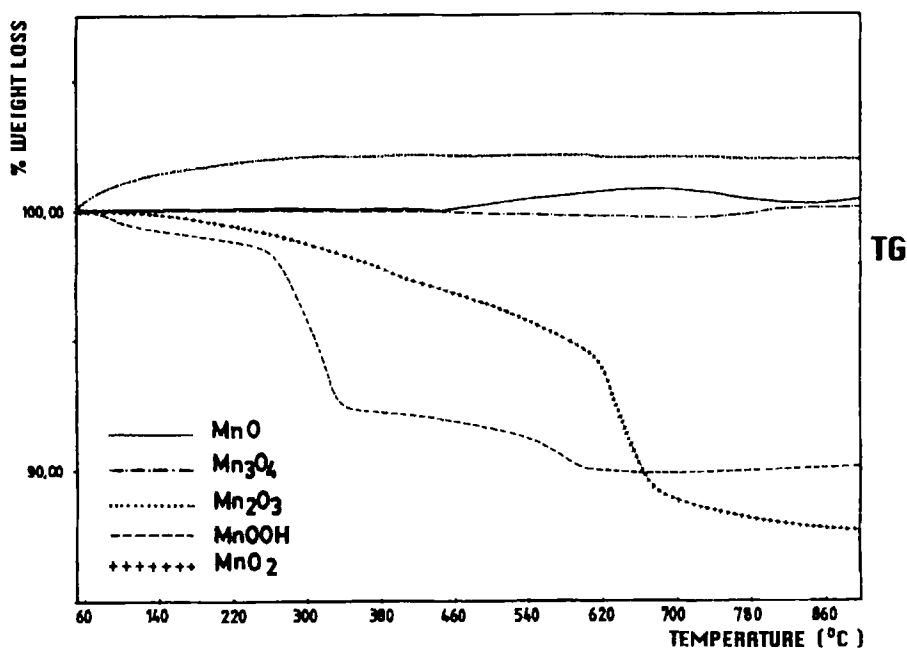
Fig. 1 TG curves for several manganese oxides in inert atmosphere

This transition plays an important role to know the electrochemical capacity when these compounds are applied as depolarizing material in primary cells. Freeman et al. [11] have shown that manganese oxides samples with lower peak temperatures for decomposition to Mn_2O_3 have high battery activity. For the studied oxides, both MnOOH and MnO_2 show this transition, although it occurs in high extent for manganese dioxide.

Table 1 Structural characteristics of the prepared manganese oxides, identified by comparing the experimental results with the reference data of XRD

Oxide	Structural characteristics	Reference data XRD
MnO	Manganosite: cubic system	JCPDS 7–0230
Mn_3O_4	Manganosic oxide: cubic system	JCPDS 4–0732
Mn_2O_3	Partridgeite: cubic system	JCPDS 10–69
MnOOH	Manganite: monoclinic system	JCPDS 18–805
MnO_2	Gamma manganese dioxide: tetragonal system	JCPDS 4–0779

Thermal analyses of the manganese oxides in air atmosphere have been plotted in Fig. 2. At oxidizing atmosphere, the only stable compound with tempe-
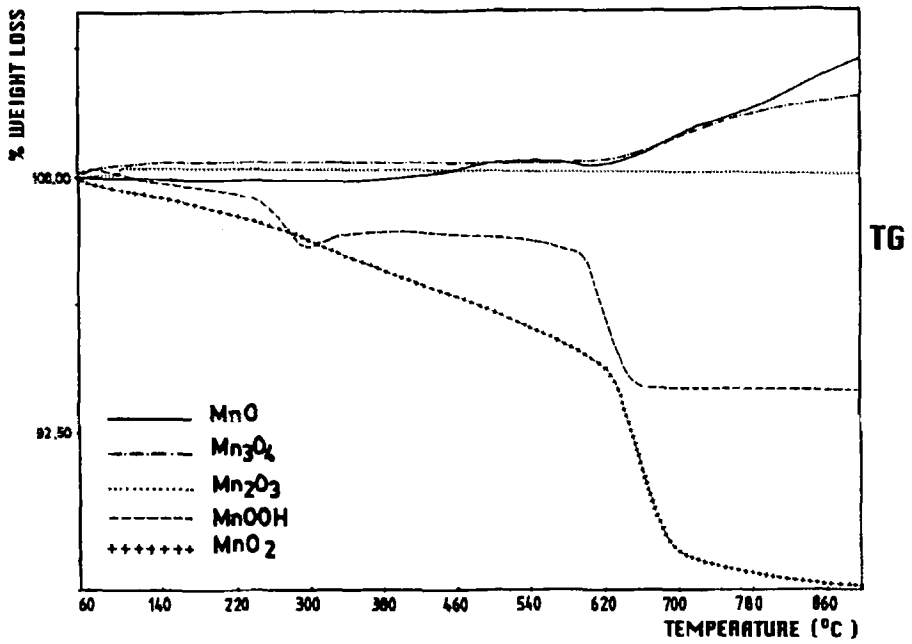
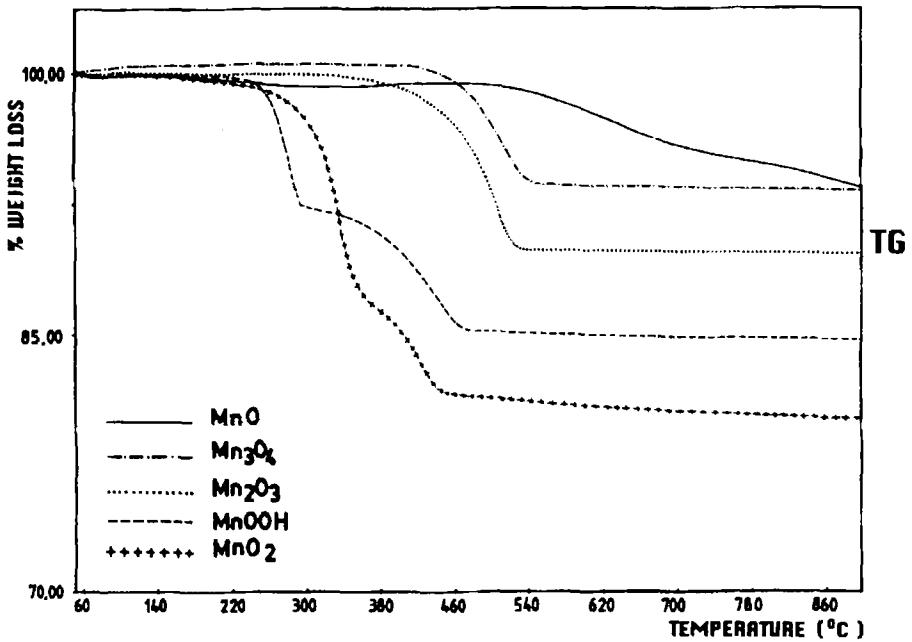Fig. 2 TG curves for several manganese oxides in air atmosphere

Fig. 3 TG curves for several manganese oxides in reducing atmosphere

rature increase is Mn_2O_3. The oxygen presence affects to the equilibrium trans-
formations of some oxides into the other [12]. So, MnO begins to oxidize at
630°C. It shows an increase of weight around 3.2%. This percentage probably
increases at higher temperatures, because of the weight loss is lower to the
stoichiometric one. Analogous behaviour is observed for the Mn_3O_4, although
the weight loss observed is lower, 2.1%. The MnOOH TG-curve is very af-
fected by the presence of oxygen. The first stage, with a weight loss of 1.3%
produce MnO_2. For the same temperatures in inert atmosphere, the percentage
obtained was 7.9%. Afterwards, in the next step, it transforms to Mn_2O_3 at tem-
peratures close to 600°C. The weight loss associated is 4.4%. For this
transition, in inert atmosphere, the weight loss was of 2.2%. In O_2 presence,
the reaction is favoured. The behaviour of MnO_2 is not affected by the oxygen
existence, due to the weight loss is equal in both atmospheres.

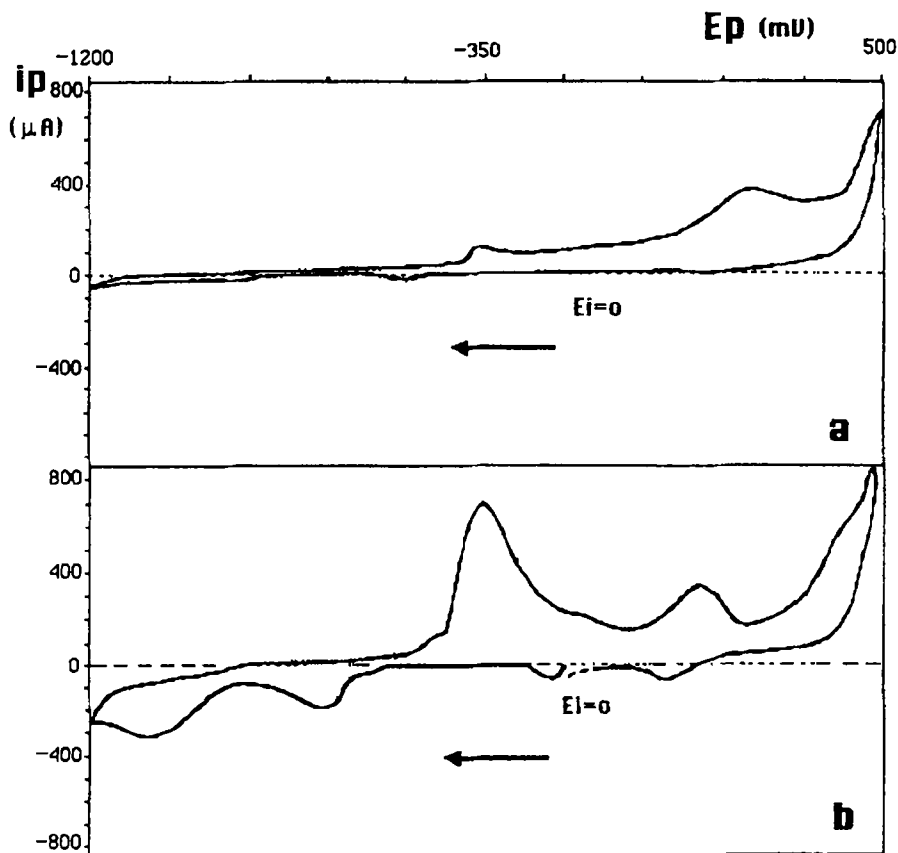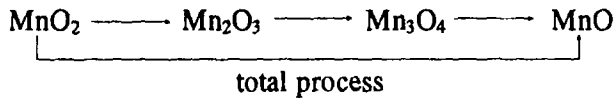Fig. 4 First cyclic voltammogram with a solid weight (1.00 mg) and a scanning rate
(0.25 mV s^{-1}) corresponding to: a) MnO, b) MnOOH

The reduction process of manganese oxides is a complex mechanism in which several stages are involved. The temperature of each stage depends on the preparation conditions, the structural properties of the oxides and the operational parameters during reduction. Manganese species reduction can be described in the way:

$$MnO_2 \longrightarrow Mn_2O_3 \longrightarrow Mn_3O_4 \longrightarrow MnO$$

total process

High stoichiometric oxides tend to give the lower stoichiometry compound, such as MnO. It is the most stable manganese oxide. In Fig. 3 have been represented TG curves of the studied compounds in reducing atmosphere. For the Mn_2O_3 and the Mn_3O_4, the reduction to MnO takes place next to 500°C. The reduction of MnOOH occurs in two stages: the first stage, at 280°C, and the
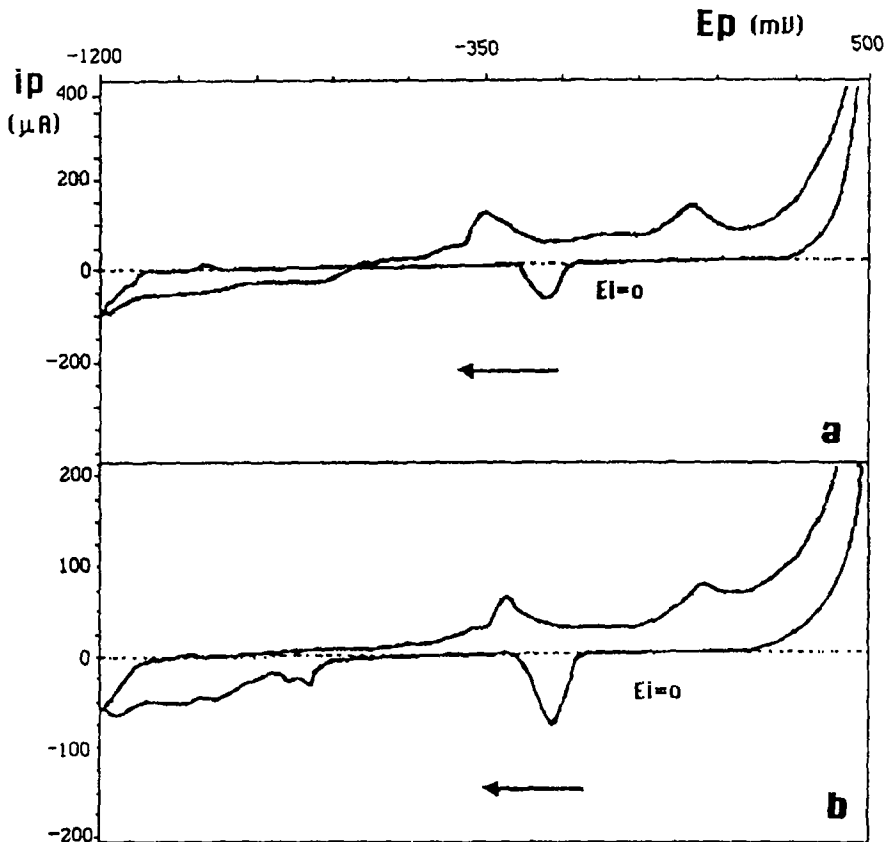

Fig. 5 First cyclic voltammogram with a solid weight (1.00 mg) and a scanning rate (0.25 mV s^{-1}) corresponding to: a) Mn_2O_3, b) Mn_3O_4
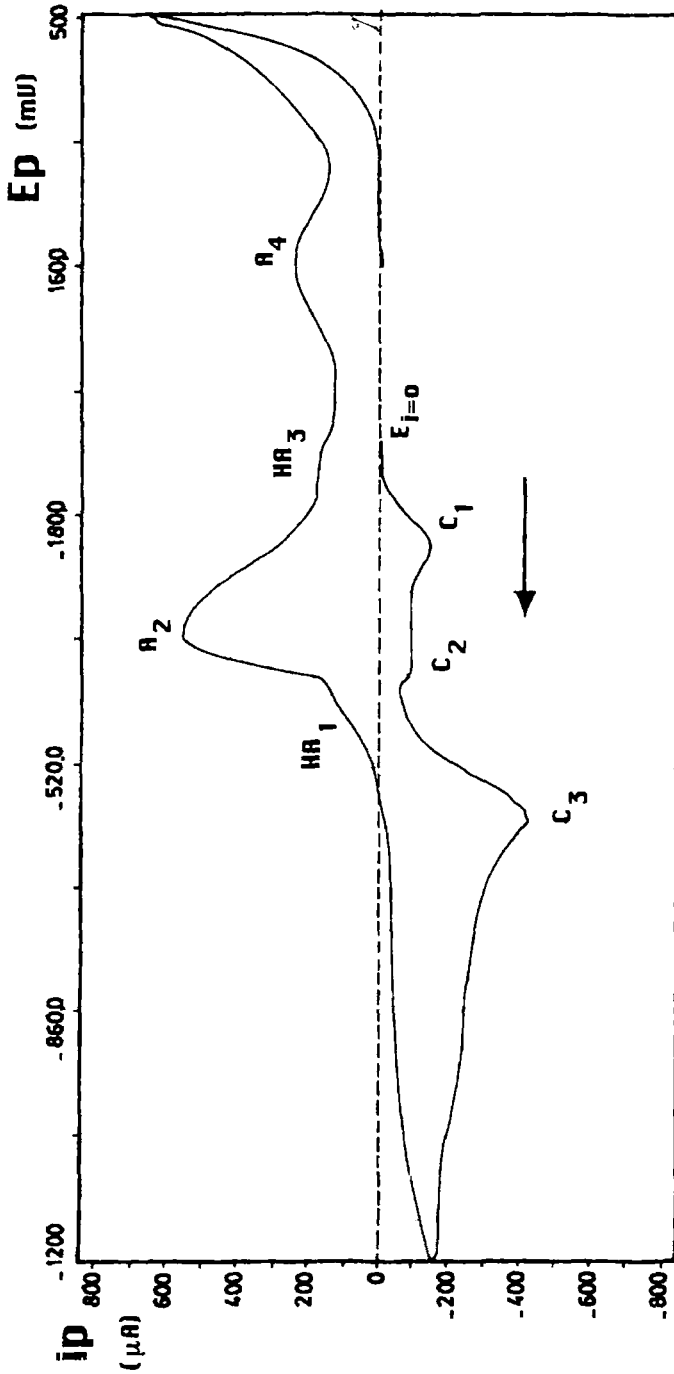
Fig. 6 First cyclic voltammogram of natural manganese dioxide: MnO_2 weight (1.00 mg), scanning rate (0.25 mV s^{-1})

second at 440°C. In the natural MnO_2, the two steps are close, showing a peak at 330°C and the other at 400°C. The reduction temperature is increasing as the stability of the oxide is higher. The obtained sequence, from lower to higher temperature is:

$$MnO > Mn_3O_4 \approx Mn_2O_3 > MnOOH > MnO_2$$
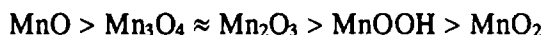
In order to evaluate the electrochemical performance of these compounds, cyclic voltammetry technique was used. Voltammetric curves were obtained using a very low scanning rate (0.25 mV s^{-1}). The electroactivity range was very large, from –1200 mV up to +500 mV. MnO shows no appreciable reduction peaks in our experimental conditions (Fig. 4a). The voltammetric study of the manganese oxyhydroxide and the lower manganese oxides (Mn_2O_3, Mn_3O_4) is respectively represented in Figs 4b, 5a and 5b. The voltammetric curves showed low intensity peaks in cathodic segment. It is probably related to the high stability of these oxides. The curves are simpler than NMD one. The oxygen reduction peak appears about –200 mV, exclude in MnO case, because it is a reducing substance. Oxygen is trapped into graphite during carbon paste preparation.

Except for MnO that is not reduced, the behaviour of the other studied compounds is similar in the anodic scan. Only the peaks intensity change with the manganese oxide type, due to the different crystalline structure. By this reason, Mn_2O_3 and Mn_3O_4 (Fig. 5a–5b), which belong to the cubic system showed identical oxidation curves.

Figure 6 illustrates first cathodic-anodic cyclic voltammogram for 1.00 mg of solid NMD. It was obtained from –30 mV up to –1200 mV and reverse scan towards +500 mV. We observed three cathodic peaks and two anodic peaks: C_1 (–228 mV), C_2 (–390 mV), C_3 (–597 mV), A_2 (–347 mV) and A_4 (+160 mV). Around A_2 peak appeared two shoulders: HA_1 (–411 mV) and HA_3 (–143 mV). In the second cathodic scan only two peaks C_2 and C_3, were observed. Only the reduction peak C_3 was observed in subsequent cycles; it is the characteristic peak of the depolarizing capacity of different polymorphic forms of MnO_2 and it is only appreciated in the curve of NMD, not in the curves of the other studied oxides.

The NMD electrochemical behavior shows good depolarizing capacity which confirms the predictions from transition of MnO_2 to Mn_2O_3 obtained from the thermal curves.

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