

# Electrochemical dissolution of $\text{Mn}_3\text{O}_4$ in acid solutions

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**Abstract** The present study deals with the electrochemical reductive dissolution of  $\text{Mn}_3\text{O}_4$ , which was added to carbon-paste electroactive electrodes (CPEEs) in acid solutions. It was found that in the experimental conditions the thermodynamically stable form of manganese was  $\text{Mn}_{\text{aq}}^{2+}$ . Kinetic features of the electrochemical reductive dissolution of  $\text{Mn}_3\text{O}_4$ , which was realized under potential cycling conditions (+1.0 V → -0.7 V → +1.0 V), were determined by the electrode polarization direction. It was shown that the cathodic reduction of  $\text{Mn}_3\text{O}_4$  was accomplished in three stages. Manganese was dissolved in the supporting solution only at the third stage. The first two stages involved solid-phase reactions. The anodic cycling stage included an active dissolution of  $\text{Mn}_3\text{O}_4$  and the lower manganese oxide (MnO) accumulated on the electrode surface during the cathodic reduction.

**Keywords** Hausmannite · Voltammetry · Reductive dissolution

## Introduction

It is known [1] that kinetic parameters of oxidation-reduction reactions can change drastically during magnetic phase transitions in oxides. Analogous effects may be expected to occur during structural phase transformations of

different types in oxide systems containing orbital-degenerate and mixed-valence 3d ions. Objects of study that appear to be most pertinent in this respect are  $\text{Mn}_3\text{O}_4$ -based oxides, which are characterized by all-time large Jahn–Teller deformations capable of affecting the rate of electrode processes. It was shown [2] that distortions of the crystal lattice induced by the Jahn–Teller effect are crucial for the behavior of electrochemical parameters in the  $\text{Co}_x\text{Mn}_{3-x}\text{O}_4$  system. To gain a deeper insight into processes taking place in such complex systems, we think it would be reasonable analyzing properties of their basic components. The present study has been concerned with the electrochemical behavior of  $\beta\text{-Mn}_3\text{O}_4$  in acid solutions. The obtained results may present independent interest as electrochemical studies are generally focused on  $\text{Mn}_2\text{O}_3$  and  $\text{MnO}_2$  oxides in the Mn–O system (e.g., [3–6]).

## Experimental

Starting hausmannite samples were prepared by dissociation of the analytically pure reactive  $\text{Mn}_2\text{O}_3$  oxide during annealing at 1,100 °C in air for 1 h and quenching.

The samples were analyzed by the X-ray powder diffraction method using a DRON-3 diffractometer in the  $\text{Cu} - K_\alpha$  radiation. According to the XRD results, the synthesized samples contained one phase and had a tetrahedral structure with the lattice constants  $a=8.152(9)$  Å and  $c=9.472(2)$  Å.

The electrochemical measurements were performed using the voltammetry method with carbon-paste electroactive electrodes (CPEEs) containing an organic binder [7]. The test substance was added to CPEEs in the amount of 0.05 to 0.4 g per gram of the carbon powder made of the spectrally pure graphite “C-2”. The binder was dibutyl

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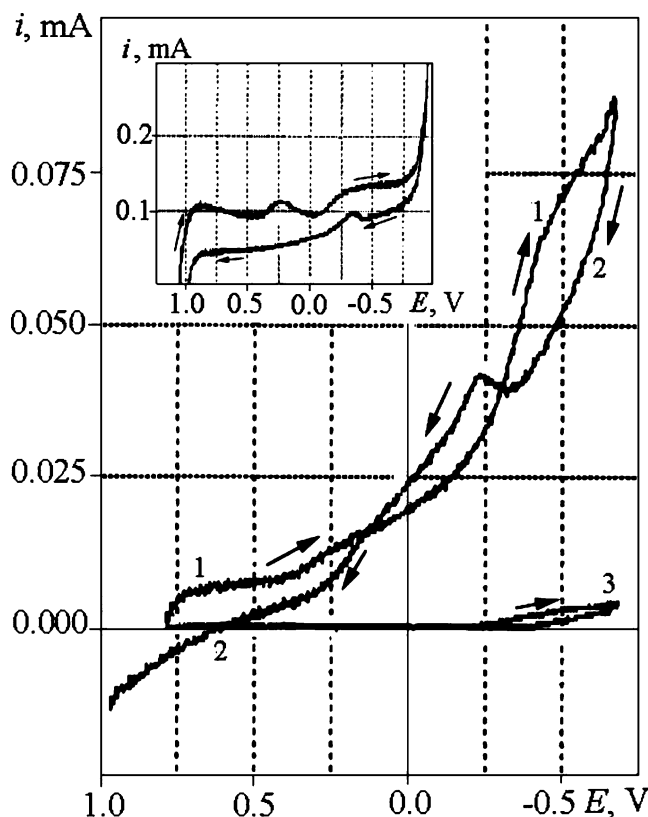
phthalate added in the amount of 0.3 ml per gram of the dry mixture. CPEEs were polarized in a PI-50-1.1 potentiostat and measured signals were brought to the PC display. A glassy-carbon crucible acted simultaneously as the auxiliary electrode and the electrolytic cell. The reference electrode was a saturated Ag/AgCl electrode of the EVL-1M1 type. Supporting electrolyte solutions were prepared of extra-pure and chemically pure reagents and triply distilled water. The potential scan rate ( $\nu$ ) was 0.5 to 500  $\text{mV s}^{-1}$  in the potentiodynamic regime. The measurements were performed in air at room temperature over the potential range between  $-0.7$  and  $+0.8$  V, when the carbon paste was electrically inactive and did not produce signals.

The chemical analysis of the supporting electrolyte samples was made by the method of atomic absorption spectrometry. A Hitachi-800 absorption spectrophotometer outfitted with a Mn hollow-cathode lamp was used. The procedure of sampling was performed in the following manner. Some potentials were chosen as limit points ( $+0.5$ ,  $+0.25$ ,  $0$ ,  $-0.25$ ,  $-0.5$ , and  $-0.7$  V). The voltammetry curve recorded from  $E_{\text{start}}$  up to the potential limit point. Then all the supporting electrolyte solution (40 ml) was stirred and subjected to the chemical analysis. Next, voltammogram was recorded up to another potential limit point and sampling for chemical analysis was done. Note that we tested the solution only if the shape of the voltammetry curve repeated the previous one.

## Results and discussion

Figure 1 presents a cyclic voltammogram, which was recorded during polarization of a  $\text{Mn}_3\text{O}_4$ -containing CPEE in 1 M HCl at the potential scan rate of  $10 \text{ mV s}^{-1}$ . It is seen from this figure that three stages of the oxide reduction could be discerned during the cathodic polarization of the electrode. The initial stage (from  $E_{\text{start}}=+0.8$  V up to  $\sim 0.6$  V) was characterized by a slight rise of the current until the point of transition to the next stage, which showed up, depending on particular experimental conditions, as a wave, a shelf or a clearly legible peak (see the inset in Fig. 1). A steep wave was typical of the third stage of the electrochemical process.

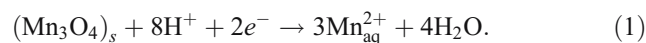
All the anodic branch of the cyclogram fitted the reductive quadrant and exhibited an anomaly in the form of the cathodic current peak at  $E \sim -0.25$  V (Fig. 1). The anomalous current (the reverse current as it was termed in [7, 8]) was observed more than once in studies of the electrochemical behavior of various systems [7–12, etc.]. However, in all those studies the anomalous current in the reverse branch of the cyclogram appeared only in the presence of a peaked response at the forward stage of the electrode polarization. Note that if the electrode was



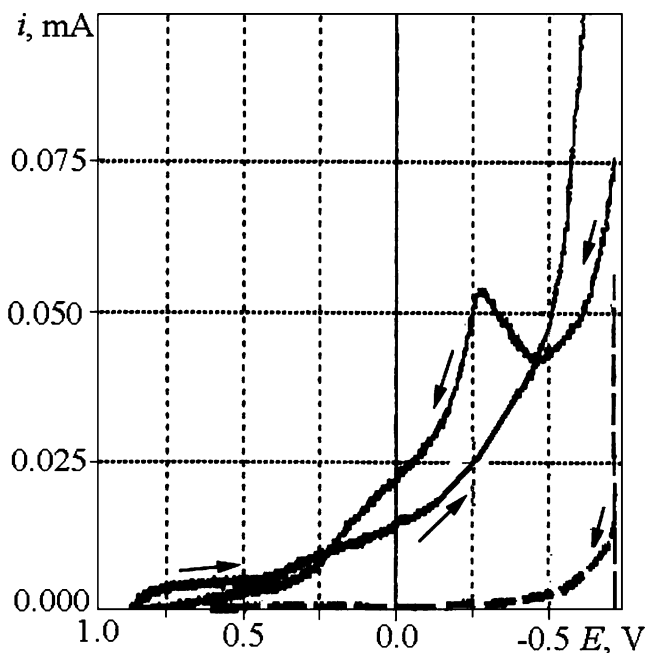
**Fig. 1** Cyclic voltammogram of  $\text{Mn}_3\text{O}_4$  in 1 M HCl at the potential scan rate of  $2 \text{ mV s}^{-1}$  from  $+0.8$  V to  $-0.7$  V (curve 1) and back (curve 2). Curve 3 background current (carbon paste signal). The inset: supporting electrolyte 6 M HCl,  $\nu=2 \text{ mV s}^{-1}$ ,  $E_{\text{start}}=1.05$  V

cycled in the reverse sequence of its polarization (anodic/cathodic) from  $E_{\text{start}}=-0.7$  V (Fig. 2), the asymmetry of the cyclogram branches was the same as in Fig. 1, but the pointed peak at the anodic stage of the process was more legible. Then one may reasonably think that, first, the irreversible reductive dissolution of  $\text{Mn}_3\text{O}_4$  took place over the range of potentials studied ( $+0.8 \dots -0.7$  V) and, second, the reductive dissolution of the hausmannite was realized by different schemes depending on the potential scan direction.

Let us consider two limiting cases. In the first case, the whole crystal dissolves and cations pass to the electrolyte solution. This situation can be described by the reaction:

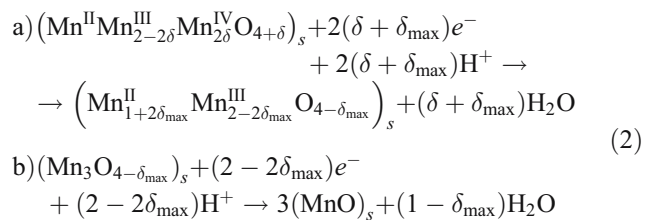


The concentration of manganese in the supporting solution should be 1/3 larger than the concentration of reduced Mn(III) calculated using the electrochemical equivalent of the passed charge. In the second case, electrochemical reduction of the oxide is accompanied by evolving of cations to the contacting solution. Taking into account that hausmannite has two-sided homogeneity range by oxygen about stoichiometric compound  $\text{Mn}_3\text{O}_4$  [13–16],



**Fig. 2** Cyclic voltammogram of  $Mn_3O_4$  in 1 M HCl at the potential scan rate of  $2 \text{ mV s}^{-1}$  from  $-0.7 \text{ V}$  to  $+0.8 \text{ V}$  and back to  $-0.7 \text{ V}$ . Dotted line shows background current

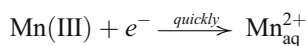
this situation can be realized by following a two-stage process:



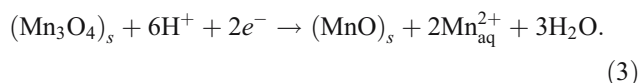
Equation 2a corresponds to proceeding of solid phase reaction in homogeneity range of the oxide  $Mn_3O_{4\pm\delta}$ . According to Eq. 2b the lower oxide is formed as an independent solid phase.

By analogy with [17, 18], let us assume that Mn(II) ions formed on the surface by reduction of Mn(III) are in a

higher reactive state than structural Mn(II) ions and, therefore, evolve to the solution more readily [19]:



Then, we obtain an intermediate expression:



In this case, structural Mn(II) ions form an independent faintly soluble MnO solid phase. Hence, the manganese concentration in the solution corresponds to the concentration of reduced Mn(III).

Results of the quantitative chemical analysis of the supporting solution samples taken at boundary points of the scan range ( $+0.8$  and  $-0.7 \text{ V}$ ) in different regimes of polarization of the  $Mn_3O_4$  electrode are compared in Table 1. The quantity  $R$  is defined by the ratio [20]:

$$R = \frac{\text{Concentration of reduced Mn}^{III} \text{ (electrochemical equivalent)}}{\text{Concentration of Mn}_{\text{aq}}^{2+} \text{ in the solution (chemical analysis)}} \tag{4}$$

It is seen from Table 1 that in the cycling regime the  $R$  value at the cathodic stage (no. 1) was a little larger than the theoretical value equal to 1 for the reductive dissolution (3). So, some newly formed Mn(II) cations stayed on the crystal surface. During the return trace (No. 2 in Table 1) the  $R$  value was, on the contrary, much smaller than the theoretical value equal to 0.667 for the process (1). This was an indication that the anodic stage of cycling involved an active dissolution of the lower manganese oxide (MnO) accumulated on the electrode surface during the cathodic reduction.

The resulting  $R$  value, which combined the phenomena in the forward and reverse half cycles, approached very closely the theoretical value for the reaction (1).

An analogous behavior was observed [20] during the electrochemical dissolution of the magnetite ( $Fe_3O_4$ ). This behavior was explained by the formation of a passivating layer formed by Fe(II) ions remaining on the crystal

**Table 1** Chemical analysis data

	Scan rate, (mVs <sup>-1</sup> )	Scan regime	Potential range (V)	Q (mC)	Amount of reduced Mn(III), (mg l <sup>-1</sup> )	Concentration of Mn <sub>aq</sub> <sup>2+</sup> in the solution (mg l <sup>-1</sup> )	R
1	2	Cycling	+0.8→-0.7	24.80	0.353	0.304	1.16
2	-0.7→+0.8		31.62	0.450	0.890	0.51	
3	+0.8→-0.7 →+0.8		56.42	0.803	1.194	0.67	
4	2	Anodic	-0.7→+0.8	25.60	0.365	0.550	0.66
5	5	polarization	-0.7→+0.8	8.43	0.120	0.180	0.67

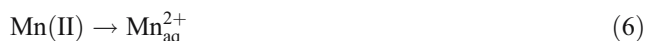
surface. However, the observed difference in our results, which are numbered 1, 2, and 3 in the table, cannot be explained in terms of the passivation mechanism, which suggests a quick drop of the current (down to zero in some cases) in the descending branch of the peak. It is seen from Fig. 1 that the cathodic branch of the cyclogram for  $\text{Mn}_3\text{O}_4$  is a continuously ascending line.

Let us consider the dynamics of the manganese concentration ( $c$ ) in the supporting solution throughout the potential scan range (Fig. 3). This observation can provide additional information about the proceeding processes. In the cathodic half-cycle manganese cations do not evolve to the contacting solution nearly until the onset of the steep cathodic wave. Then the  $\text{Mn}_{\text{aq}}^{2+}$  concentration increases monotonically. In the subsequent anodic half cycle the concentration of manganese cations in the electrolyte continues growing, at a higher rate at that.

The analysis of the available data (Table 1 and Fig. 3) suggests that the electrochemical stage

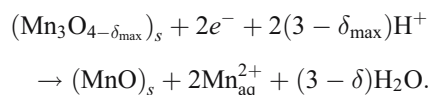


and the subsequent chemical stage



of the electrode process have different kinetics. The reactivity/rate constant ratio for these stages depends on the scan direction and the instant potential value. This statement can be illustrated by  $c$ - $Q$  curves (Fig. 4). Theoretical  $c$ - $Q$  dependences for the reactions 1–3 are shown as straight lines with appropriate indices in Fig. 4. It is seen that the figurative point of the electrode process describes a complicated path in the space of  $c$ - $Q$  parameters. At the initial stage of the process the figurative point follows the line (2; see the inset in Fig. 4), suggesting that a solid-phase reaction proceeds.

As low-oxygen boundary of the homogeneity region is reached ( $\delta_{\text{max}}$ ), the further reduction of the oxide leads to transformation of the crystal lattice by the scheme (Eq. 3). The figurative point of the process correspondingly follows the straight line (3; Fig. 4). Taking into account the defect structure of the hausmannite, Eq. 3 can be rewritten as



When the scan direction was reversed (to anodic), the reductive dissolution of  $\text{Mn}_3\text{O}_4$  continued, but by the scheme (Eq. 1). Structural Mn(II) cations accumulated on the electrode surface dissolved simultaneously. Correspondingly, the figurative point of the total process crossed the mixed (electrochemical + chemical) dissolution region and

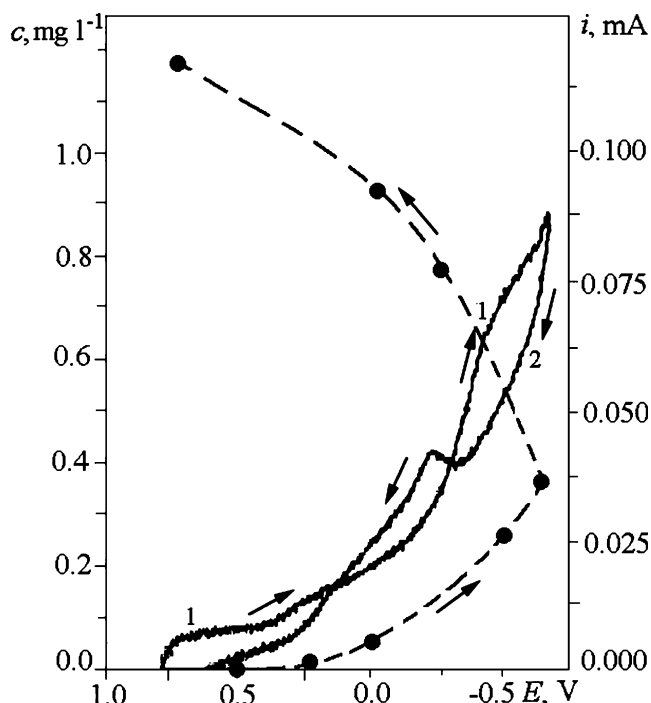


Fig. 3 Variation dynamics of the concentration of  $\text{Mn}_{\text{aq}}^{2+}$  ions in the supporting electrolyte during cyclic scanning at a rate of  $2 \text{ mV s}^{-1}$

by the end of the cycle the system reached the state when all manganese involved in the process passed to the electrolyte solution.

To gain better understanding, we consider the anodic stage of the process in its pure form by scanning the potential from  $E_{\text{start}} = -0.7 \text{ V}$  in the positive direction. Figure 5 presents experimental results in the  $c$ - $Q$  coordinates for two potential scan rates ( $5$  and  $2 \text{ mV s}^{-1}$ ) against the corresponding voltammograms. As can be seen, at  $v_{\text{sc}} =$

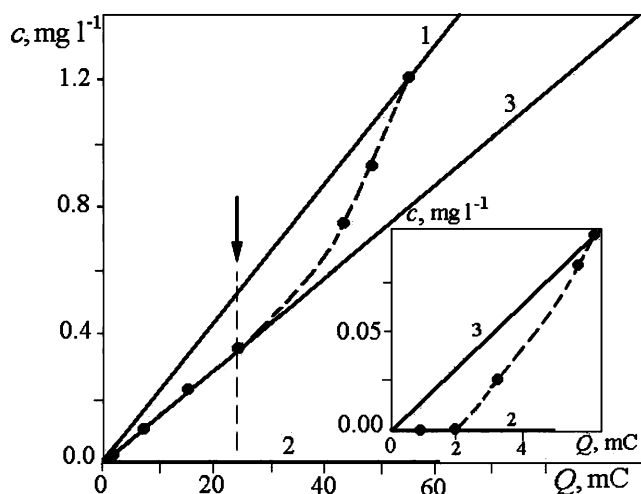
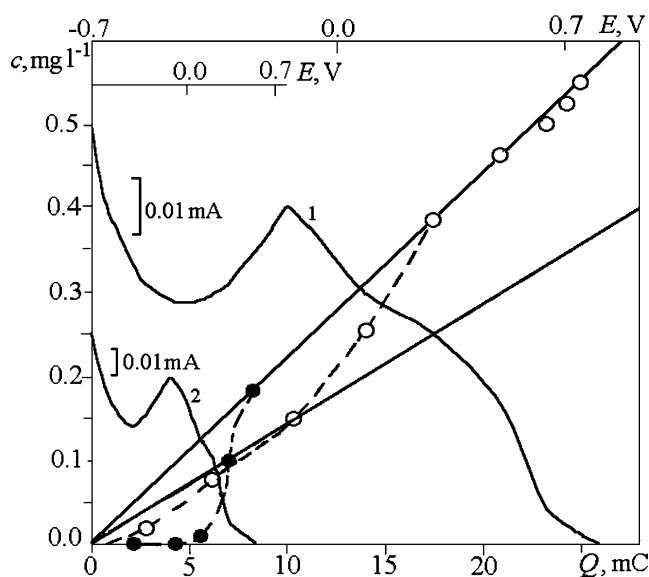


Fig. 4 Concentration of manganese ions in the electrolyte solution vs the passed charged during cyclic scanning of the potential. Straight lines 1, 2, and 3 show theoretical  $c$ - $Q$  dependence for the reactions (1), (2), (3), correspondingly. Arrow indicates the charge related to the end of the cathodic half cycle



**Fig. 5** Concentration of manganese ions in the electrolyte solution vs the passed charge from  $-0.7$  V to  $+0.8$  V at the potential scan rate of  $2 \text{ mV s}^{-1}$  ( $\circ$ , corresponding voltammogram 1) and  $5 \text{ mV s}^{-1}$  ( $\bullet$ , corresponding voltammogram 2). Straight lines have the same meaning as in Fig. 4

$5 \text{ mV s}^{-1}$  the initial stage, which was characterized by a pointed response in the  $i/E$  curve, a solid-phase electrode reaction proceeded by scheme (Eq. 2). The quantitative chemical analysis did not reveal manganese cations in the supporting solution. That indicates a low rate of their detachment from the reaction surface at this stage of the electrode polarization. Over the range of positive potentials, the chemical stage of the reductive dissolution was accelerated so that at the end the process proceeded in the kinetic regime (the dissolution rate was much higher than the formation rate of Mn(II)).

If the potential was scanned slower, the chemical stage appeared earlier in the electrochemical process. According to the chemical analysis, at  $v_{sc}=2 \text{ mV s}^{-1}$  a remarkable concentration of  $\text{Mn}_{aq}^{2+}$  was found in the solution already at the very beginning of the electrode polarization. By the moment the potential turned to zero, the electrode reaction changed to a purely kinetic regime.

The above experimental facts can be summarized as follows:

1. The electrochemical reductive dissolution of  $\text{Mn}_3\text{O}_4$  is an irreversible multistage process. The thermodynamically stable form of manganese in the experimental conditions is  $\text{Mn}_{aq}^{2+}$ .
2. Kinetic peculiarities of the electrochemical reduction during polarization of the  $\text{Mn}_3\text{O}_4$  electrode at a constantly varying potential are determined by the potential scan direction (cathodic-anodic). If the external potential is shifted to the negative side, the electrochemical stage (2) of the electrode process accelerates, whereas the chemical stage (detachment

of manganese cations from the reaction surface and their diffusion to the bulk of the electrolyte) is retarded. When the potential is scanned in the opposite (anodic) direction, the reverse effect is observed: the chemical stage accelerates and the electrochemical stage is retarded. Observed peculiarities in the behavior of the system under consideration can be explained in terms of the theory of charged-particles diffusion in an electric field [21]. When the electrode is polarized in the cathodic direction, the increase of the overvoltage causes the acceleration of the electrochemical stage. At the same time, the electric field, whose intensity increases with the cathodic overvoltage, inhibits the detachment of charged particles ( $\text{Mn}^{2+}$ ) from the reaction surface and their diffusion to the bulk of the electrolyte. Therefore, most reactive (newly formed) Mn(II) cations were only dissolved at the cathodic stage of the electrode process. It is noteworthy that at the end of the cathodic polarization (before the potential scan direction was reversed) the retardation effect of the electric field was so large that even highly reactive manganese (II) cations stayed on the electrode surface (see Fig. 4 and row 1 in Table 1).

The opposite picture was observed after change of the potential scan direction from negative to positive (at the anodic stage of cycling). The continuously attenuating retardation effect of the electric field on the chemical stage of the electrode process was the factor responsible for the quick change of the system to the kinetic regime and the realization of scheme (Eq. 1), when the whole  $\text{Mn}_3\text{O}_4$  crystal dissolved and all Mn cations passed to the electrolyte solution.

It should be mentioned that in Grygar's opinion [22] this electrostatic interpretation of the chemical stage (6) is not irreproachable. Nevertheless, he had to acknowledge that the only explanation for the pointed shape of  $K(E)$  in  $\text{Fe}_3\text{O}_4$  was a rather rare (unusual) mechanism for removal of the reaction product from the reaction layer surface by diffusion through the electrified diffusion layer.

## Conclusion

The electrochemical behavior of the hausmannite in an acid medium (HCl) was analyzed. It was shown that an irreversible reaction of the reductive dissolution of  $\text{Mn}_3\text{O}_4$  took place irrespectively of the potential scan direction (cathodic/anodic) over the space of parameters of the electrode process studied. In these conditions the thermodynamically stable form of manganese was  $\text{Mn}_{aq}^{2+}$ .

The electrochemical (reduction of Mn(III) to Mn(II)) and subsequent chemical (dissolution of MnO in the form of



$\text{Mn}^{2+}_{aq}$ ) stages had different kinetics, which depended on the potential scan rate and direction during the cyclic polarization of the electrode. The observed features of the electrode processes could be explained in terms of the theory of charged-particles diffusion in an electric field.

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