ResearchGate

See discussions, stats, and author profiles for this publication at: https://www.researchgate.net/publication/226037405

Kinetics of anodic formation and cathodic reduction of MnO2 in the sulfate electrolyte solutions

Article *in* Russian Journal of Electrochemistry · January 2008

DOI: 10.1134/S1023193508110165

CITATIONS
11

READS
162

5 authors, including:

Sviatoslav Kirillov
Joint Department of Electrochemical Energy Systems
114 PUBLICATIONS **1,112** CITATIONS

SEE PROFILE

Dali Dzanashvili
Ivane Javakhishvili Tbilisi State University
26 PUBLICATIONS **136** CITATIONS

SEE PROFILE

Some of the authors of this publication are also working on these related projects:

Project Condensed Phosphates of mono- and polyvalent metals View project

Project Method development for the determination of polyvalent metals in double condensed phosphates View project

All content following this page was uploaded by Sviatoslav Kirillov on 22 May 2014.

The user has requested enhancement of the downloaded file.

ISSN 1023-1935, Russian Journal of Electrochemistry, 2008, Vol. 44, No. 11, pp. 1299–1306. © Pleiades Publishing, Ltd. 2008.
Original Russian Text © O.G. Tsiklauri, T.A. Marsagishvili, G.S. Tsurtsumiya, S.A. Kirillov, D.I. Dzanashvili, 2008, published in Elektrokhimiya, 2008, Vol. 44, No. 11, pp. 1395–1403.

Kinetics of Anodic Formation and Cathodic Reduction of MnO_2 in the Sulfate Electrolyte Solutions

O. G. Tsiklauri[a], T. A. Marsagishvili[a,z], G. S. Tsurtsumiya[a], S. A. Kirillov[b], and D. I. Dzanashvili[a]

[a]*Agladze Institute of Inorganic Chemistry and Electrochemistry, Tbilisi, Georgia*

[b]*Institute of Sorption and Endoecology, National Academy of Sciences of Ukraine, Kiev, Ukraine*

Received September 4, 2006; in final form, August 31, 2007

Abstract—The anodic formation of manganese dioxide is studied voltammetrically in a wide range of potential scan rate (V = 0.001–8 V/s). Using the diagnostic criteria of cronovoltammetric method, based on the original experimental data, the mechanism of electrooxidation of manganese ions in the acidic medium with subsequent reaction of disproportionation of the product of irreversible electrode reaction and hydrolysis yielding manganese dioxide is proposed. The kinetics of cathodic reduction of electrolytic manganese dioxide in the 0.5 M Na_2SO_4 solution is studied under the steady-state and non-steady-state potentiodynamic polarization conditions. From the experimental data, it is found that, in the acidic medium (pH 1–3), the mechanism of the electrode process changes depending on the cathodic potential scan rate: at the scan rate $V < 0.5$ V/s, MnOOH forms via one-electron transition leading, in its turn, to the partial deactivation of electrode surface with subsequent disproportionation of manganite. At the relatively high potential scan rates, manganite has no time to form, and the two-stage reduction via one-electron transitions at each stage is well pronounced. The parameters of the electrode processes are calculated.

Key words: manganese dioxide, manganite, cyclic voltammetry, mechanism of electrooxidation of manganese ions, heterogeneous constant of charge transfer rate, transfer coefficient, free energy of charge transfer, constant of disproportionation

DOI: 10.1134/S1023193508110165

INTRODUCTION

The process of manganese dioxide production is of great interest to the researchers, because it is widely used in the power sources and other fields of engineering. The study of kinetics of electrochemical production of manganese dioxide provides new information on its peculiarities and enables one to fabricate this valuable product with prescribed properties.

Various mechanisms of cathodic reduction of MnO_2 depending both on the electrolyte composition and on the rate of variation of polarizing voltage were proposed [1–10]. However, the literature data both on the anodic formation of MnO_2 and on its cathodic reduction are contradictory.

In [1–6], the reduction of γ-MnO_2 powder in the acidic solutions (pH 1–4) was studied using the method of linear potential scan. In the acidic solutions, the two-stage reduction with the consumption of one electron at each stage was observed in the voltammograms. At the first stage, manganite forms. In [7], another mechanism of electrochemical reduction of MnO_2 in the 2 M H_2SO_4 solution was studied and proposed. According to [7], after the manganite formation, the chemical reactions proceed at the first stage: (1) the dissolution of manganite with the formation of Mn^{3+} and (2) the disproportionation of Mn^{3+} with the formation of Mn^{2+} and MnO_2. The second stage corresponds to the reduction of manganese dioxide, which has deposited by the disproportionation reaction; as a result, manganite forms again. However, why deposited MnO_2 is reduced at more negative potential than the main material is not clear from this mechanism. The electrochemical reduction of MnO_2 in the acidic solutions was studied in more detail in [8–10]. Three peaks were observed in the voltammograms of cathodic process (the potential scan rate was 0.001–1 V/min). In 0.0125–1.25 M sulfuric acid, two peaks were observed; the third peak between them emerged in the concentrated (3.75–7.5 M) H_2SO_4 solution. The rise of this peak was related to the reduction of Mn^{3+}, which had formed at the potential of the first peak. The character of the second peak strongly depends on the substrate nature. As is seen from the brief literature review, rather contradictory versions of the mechanism of MnO_2 cathodic reduction were proposed depending both on the electrolyte composition and on the polarizing voltage scan rate.

The anodic deposition of MnO_2 is a complex process involving several chemical and electrochemical stages. The net reaction of MnO_2 formation from the

[z] Corresponding author: tmars@geo.net.ge (T.A. Marsagishvili).

sulfuric acid solutions proceeds according to the following equation:

$$Mn^{2+} + 2H_2O - 2e \longrightarrow MnO_2 + 4H^+. \quad (1)$$

Different, often contradictory views on the mechanism of this reaction are available from the literature [11]. In [12], the mechanism of anodic formation of MnO_2 as a result of Mn^{2+} oxidation to Mn^{4+} ions, which, then, are hydrolyzed to H_2MnO_3, was proposed. The authors of [13] do not agree with this viewpoint. Based on the data on the variations in the platinum anode potentials with time at the constant current density for the solutions containing Mn^{2+} or Mn^{3+} ions, and also on the data on the absorption spectra of solutions in the anodic area, they concluded that not permanganic acid, but Mn^{3+} ions are the primary product of oxidation. At the second stage, Mn^{3+} ions are electrochemically oxidized to Mn^{4+} in the concentrated acid and disproportionate to Mn^{2+} and Mn^{4+} in the dilute acid. Then, the hydrolysis of Mn^{4+} with the formation of MnO_2 takes place. This mechanism of electrodeposition was studied in more detail in [14, 15]. A series of studies concerning this problem was performed by Japanese researchers [6, 16–19] using a rotating disk electrode. It was indicated [16] that the mechanism of anodic deposition of MnO_2 changes depending on the anodic potential scan rate. At low potential scan rates, the two-stage voltammetric characteristic of anodic process was recorded, whereas at high scan rates ($V = 12$ V/s), a single wave was observed, which, in the authors' opinion, corresponded to the one-electron electrode reaction.

In [20], it was proposed that only one-electron reaction is realized on the anode and, then, instantaneous disproportionation of Mn^{3+} with the formation of Mn^{4+} takes place. In the weakly acidic medium, Mn^{4+} is hydrolyzed yielding MnO_2. Mn^{3+} is hydrolyzed to a smaller extent. The rate of hydrolytic reaction depends on the temperature of solution. These processes affect the physical and chemical properties of MnO_2. In [21, 22], it was reported that the anodic limiting current is independent of the microelectrode rotation rate and, consequently, is not diffusion. The work of Latvian researchers [23] should be mentioned. The scheme of anodic production of MnO_2, which was proposed in [23], involves the oxidation of Mn^{2+} to Mn^{4+} in one stage, slow hydrolysis of Mn^{4+} to MnO_2, and the formation of Mn^{3+} as a result of reaction of two- and four-valent manganese ions in the diffusion layer.

In [24], the mechanism of Mn^{2+} electrooxidation on a platinum electrode was studied using the chronopotentiometric method. Based on the experimental data, the authors concluded that the preceding chemical reaction and the adsorption processes were absent. The process rate was controlled by the rate of mass-transfer, which was followed by the two-electron transfer. In [25], the mechanism of dioxide formation was proposed, according to which manganese and oxygen ions cross the interface in parallel. In [26], it was shown that manganese dioxide electrodeposition proceeds through the stage of Mn^{3+} formation, which is electrochemical on platinum and proceeds via the chemisorption of Mn^{2+} ions with the formation of Mn^{3+} on manganese dioxide surface. The Mn^{3+} ions convert into MnO_2 by the reaction of disproportionation. In [27], based on the analysis of cyclic voltammograms of rotating manganese dioxide disk electrode with platinum ring, it was supposed that the reduction of MnO_2 by Mn^{2+} ions yielding manganite occurs in the heterogeneous chemical reaction in parallel with the synthesis of MnO_2 proceeding via the stages of Mn^{3+} ions formation and their disproportionation.

As is seen from the above review, different viewpoints on the mechanism and kinetics of electrochemical deposition of manganese dioxide were advanced. The majority of authors consider that three-valent manganese forms at the first stage and, then, it chemically or electrochemically converts into MnO_2. Some researchers believe that concurrent transfer of two electrons with the formation of four-valent manganese takes place and, then, the latter is subjected to the hydrolysis yielding Mn^{2+}, which is the end product. In some works, the indirect oxidation of Mn^{2+} ions was proposed. This discrepancy in views calls for further thorough investigation of manganese dioxide electrodeposition.

Based on the analysis of literature data, we decided to increase the electrode potential scan rate, to use completely the diagnostic potentialities of chronovoltammetric method, to increase the body of experimental data on the mechanism and kinetics of anodic formation and cathodic reduction of manganese dioxide in the acidic sulfate electrolyte solutions in order to propose more substantiated mechanisms of electrode processes and calculate the kinetic parameters.

EXPERIMENTAL PROCEDURE ON THE ANODIC FORMATION OF MnO_2

To prepare the working solutions, twice-recrystallized manganese sulfate and sulfuric acid and sodium sulfate of reagent grade were used. The source reagents were dissolved in twice-distilled water. Prior to the electrochemical measurements, the solution was deaerated for an hour with purified argon. The experiments were performed in the thermostated cell with separated cathodic and anodic compartments. A spiral thin platinum band was used as the auxiliary electrode. A saturated silver–chloride electrode served as the reference electrode; it was separated from the working electrode with an intermediate vessel to prevent the entry of chloride ions into the working solution. All potentials are referred to the standard hydrogen electrode.

The anodic deposition and cathodic reduction of manganese dioxide were performed in 0.5 M Na_2SO_4 + 0.1 M H_2SO_4 solution, which had been deaerated with argon at a temperature of 298 K. To obtain the reproducible data, platinum surface, on which manganese

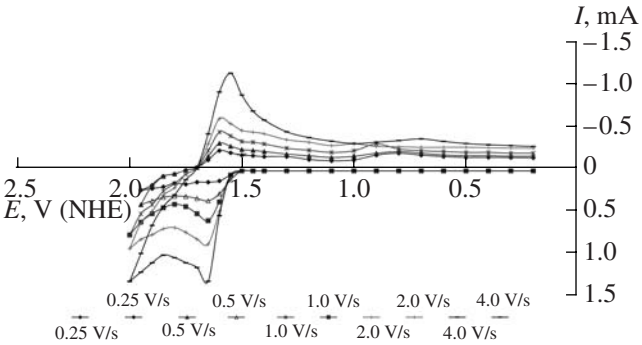

Fig. 1. Cyclic voltammograms of Mn^{2+} electrooxidation on platinum electrode in 0.5 M Na_2SO_4 + 0.005 M Mn^{2+} solution (pH 1; 298 K).

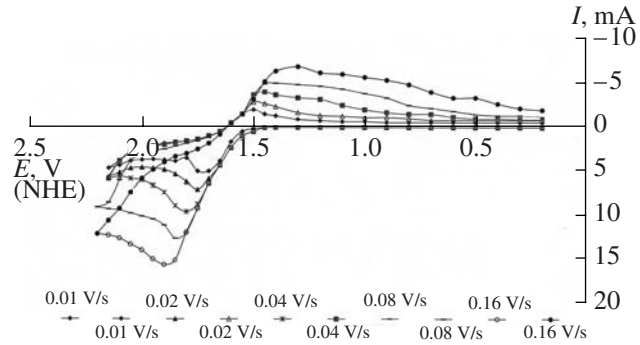

Fig. 2. Cyclic voltammograms of Mn^{2+} electrooxidation on MnO_2 electrode in 0.5 M Na_2SO_4 + 0.005 M Mn^{2+} solution (pH 1; 298 K).

dioxide was deposited, had been pretreated. The platinum wire ($\sigma = 0.018$ cm^2) was cathodically polarized at $E = 0.5$ V for 10 min with stirring of solution. When the polarization was switched off and the steady-state potential ($E_{st} = 0.02$ V) was reached, the electrode was anodically polarized at the potential of manganese dioxide deposition ($E_a = 1.2$ V) for 15 min. Then, the electrode was washed with distilled water and placed into the electrochemical cell with the test solution. After measuring each voltammogram, the working electrode was treated with hydrochloric acid in order to remove manganese dioxide from the surface and, then, the pretreatment was repeated, and manganese dioxide was deposited. The voltammograms of anodic process were measured in a wide range of potential scan rates (0.001–8 V/s). For this purpose, a PI-50-1.1 potentiostat with a PR-8 programmer and a PO-5122 mod 03 oscillographic polarograph were used.

EXPERIMENTAL RESULTS ON MnO_2 ANODIC FORMATION AND DISCUSSION

In the voltammograms of MnO_2 electrodeposition on platinum and manganese dioxide electrodes, which were measured under the potentiodynamic polarization conditions, a single peak is observed (Figs. 1 and 2), which has all specific features of irreversible non-steady-state electrochemical processes [28–30]:

(1) With increasing voltage scan rate, the potential of peak E_p shifts in the anodic direction, the peak half-width E_p–$E_{1/2}$ increases and becomes much larger than $0.059/\beta n$ (Table 1).

(2) The potential difference between the anodic and cathodic peaks is much larger than the potential difference, which is typical for reversible electrochemical reactions ($0.058/n$).

(3) The ratio between the anodic and cathodic peaks is unity only at the potential scan rates $V > 0.5$ V/s (Fig. 3).

The primary experimental data were analyzed using the known diagnostic criteria of chronovoltammetric method [29, 30]:

the transfer coefficient βn was determined from the Matsuda and Ayabe dependence:

$$E_p - E_{1/2} = 1.857RT/\beta nF = 0.048/\beta n; \quad (2)$$

the diffusion coefficient was calculated using the Delahay equation for the peak current of non-steady-state irreversible processes:

$$i_p = 2.99 \times 10^5(\beta n)^{1/2}D^{1/2}cv^{1/2}; \quad (3)$$

the heterogeneous constant of charge transfer rate k_s was determined from the dependence:

$$(E_{p/2} - E^0)\beta n + RT/F\ln\frac{\sqrt{\pi Db}}{k_2} = 0.04236. \quad (4)$$

To determine the free activation energy of charge transfer, the following equation was used:

$\Delta G = F[\beta n(E_a - E_p) - 0.059\log i_p/nc + 0.54 + 0.059 \times 10^8\rho]$ where E_a is the potential of reference electrode and ρ is the distance, to which the depolarizer approach the electrode ($\sim 4 \times 10^{-8}$ cm).

The diffusion constant χ and, correspondingly, the diffusion layer thickness δ were determined from the current densities, which were measured under the

Table 1. The kinetic transfer coefficients βn for various anode potential scan rates; pH 1, $c_{Mn^{2+}} = 1 \times 10^{-5}$ mol cm^{-3}, 298 K

V, V/s	Pt		MnO_2	
	$E_p - E_{1/2}$, V	βn	$E_p - E_{1/2}$, V	βn
0.16	0.104	0.45	0.122	0.38
0.25	0.108	0.44	0.138	0.35
0.5	0.110	0.43	0.144	0.33
1.0	0.115	0.42	0.148	0.32
2.0	0.144	0.33	0.133	0.35
4.0	0.136	0.35	0.135	0.35
8.0	0.134	0.39	0.140	0.34

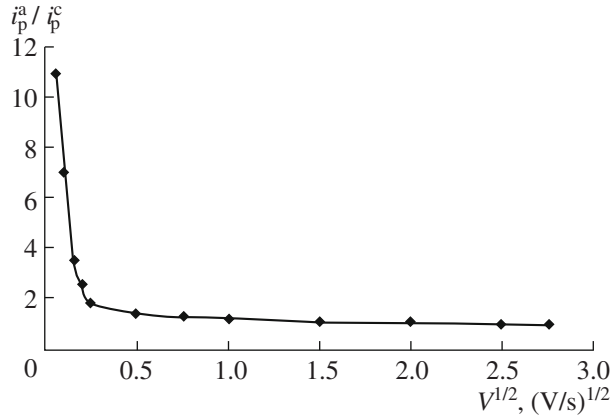

Fig. 3. Plot of i_p^a/i_p^c vs. $V^{1/2}$ for the Mn^{2+} electrooxidation on platinum electrode in 0.5 M Na_2SO_4 solution (pH 1, $c_{Mn^{2+}} = 1 \times 10^{-5}$ mol/cm^3).

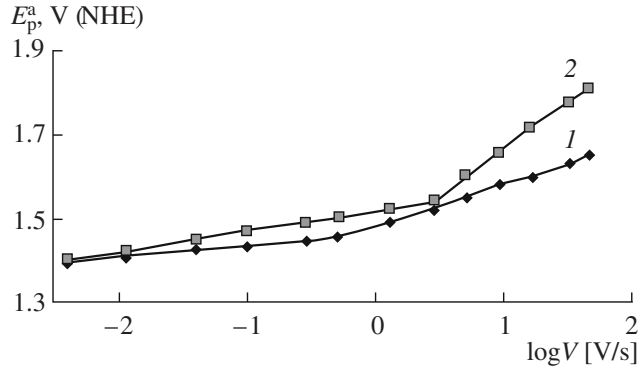

Fig. 4. Plots of E_p^a vs. $\log V$ for the Mn^{2+} electrooxidation on (*1*) platinum and (*2*) manganese dioxide electrodes in 0.5 M Na_2SO_4 solution (pH 1; $c_{Mn^{2+}} = 1 \times 10^{-5}$ mol/cm^3; 298 K).

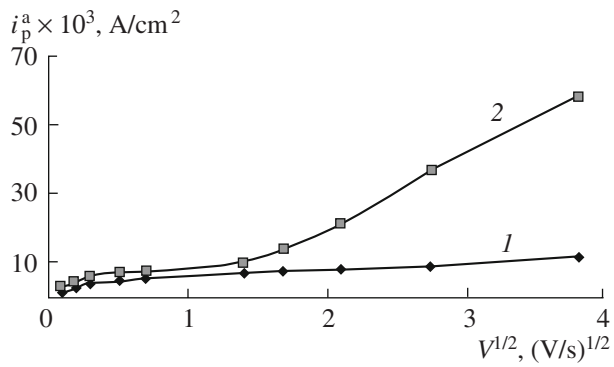

Fig. 5. Plots of i_p^a vs. $V^{1/2}$ for the Mn^{2+} electrooxidation on (*1*) platinum and (*2*) manganese dioxide electrodes in 0.5 M Na_2SO_4 solution (pH 1; $c_{Mn^{2+}} = 1 \times 10^{-5}$ mol/cm^3; 298 K).

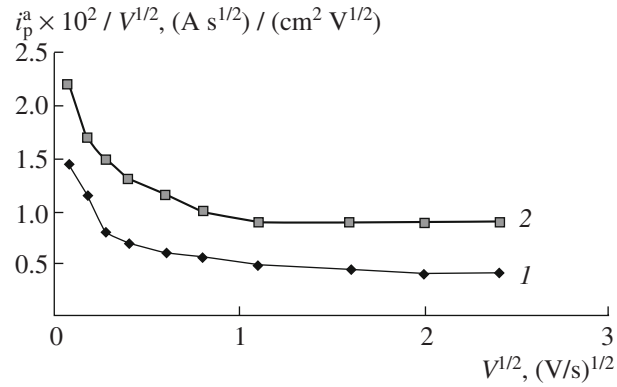

Fig. 6. Plots of $i_p^a/V^{1/2}$ vs. $V^{1/2}$ for the Mn^{2+} electrooxidation on (*1*) platinum and (*2*) manganese dioxide electrodes in 0.5 M Na_2SO_4 solution (pH 1; $c_{Mn^{2+}} = 1 \times 10^{-5}$ mol/cm^3; 298 K.

steady-state potentiodynamic conditions, by the dependence:

$$\chi = D/\delta = i_p/nFc. \quad (5)$$

The experimental data are presented on the E_p vs. $\log V$, i_p vs. $V^{1/2}$, $i_p/V^{1/2}$ vs. $V^{1/2}$ and $i_p/V^{1/2}$ vs. $\log V$ coordinates (Figs. 4–7). The shapes of the plots are similar for platinum and manganese dioxide electrodes indicating that the mechanisms of the processes are identical on both electrodes. The plots differ only in the current densities and in the potential scan rate, at which the process mechanism changes (Figs. 4 and 5). The peak height is by 1.7 times higher on the manganese dioxide electrode than on platinum electrode throughout the range of potential scan rates (Fig. 8). This can be explained by the difference in the working area due to the porosity of manganese dioxide electrode. It should be also noted that the process rate on the manganese dioxide electrode only slightly changes with the variation of the concentration of Mn^{2+} ions. According to [26], this can be explained by the adsorption of manganese ions on the manganese dioxide electrode. This is supported to some extent by the difference in the free activation energy of potential-determining stage.

A decrease in the $i_p/V^{1/2}$ ratio with increasing $V^{1/2}$ is the evidence for the presence of conjugations of chemical reaction. The diffusion coefficients, which are calculated using the Delahay equation by the $(i_p/V^{1/2})_{V \to 0}$ values, are clearly overestimated (2×10^{-4} cm^2 s^{-1}) as compared with the literature data ($D = 6 \times 10^{-6}$ cm^2 s^{-1}) [24]. The value of D, which is calculated by the $(i_p/V^{1/2})_{V \to \infty}$, value, when it becomes constant (in the diffusion mode), is 3×10^{-6} cm^2 s^{-1} approaching the literature data. This confirms the presence of subse-

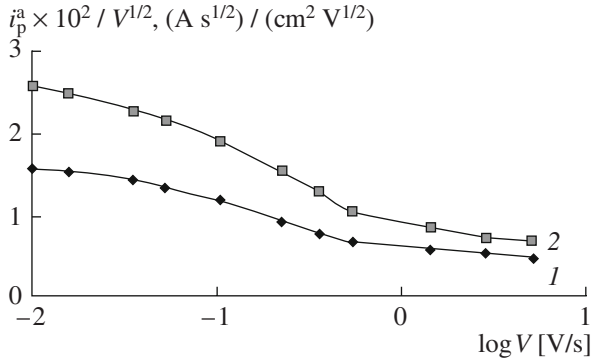

Fig. 7. Plots of $i_p^a/V^{1/2}$ vs. $\log V$ for the Mn^{2+} electrooxidation on (*1*) platinum and (*2*) manganese dioxide electrodes in 0.5 M Na_2SO_4 solution (pH 1; $c_{Mn^{2+}} = 1 \times 10^{-5}$ mol/cm^3; 298 K).

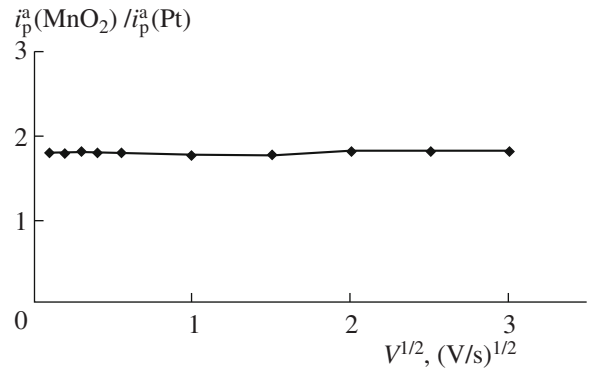

Fig. 8. Plot of $i_p^a(MnO_2)/i_p^a(Pt)$ ratio vs. $V^{1/2}$ for the Mn^{2+} electrooxidation on platinum and manganese dioxide electrodes in 0.5 M Na_2SO_4 solution (pH 1; $c_{Mn^{2+}} = 1 \times 10^{-5}$ mol/cm^3; 298 K).

quent chemical reaction of disproportionation of the product of electrode stage, when the near-electrode layer is partially supplied with Mn^{2+} ions. Obviously, this explains also the overestimated diffusion constant χ and, correspondingly, the diffusion layer thickness δ at low anodic potential scan rates (Table 2). From the plot of $i_p^a/V^{1/2}$ vs. $\log V$ (Fig. 7), the half-decay time of intermediate (three-valent manganese) and $V_{1/2}$ (the potential scan rate corresponding to the half-decay time) can be determined [31]. Taking into account that the disproportionation reaction is the second-order reaction, we can determine the disproportionation rate constant K_{DPP} by the equation $K_{DPP} = 1/\tau_{1/2}c$. At high potential scan rates, the product of electrode reaction has no time to disproportionate, and the peak height is determined only by the diffusion delivery of source species to the electrode surface. Therefore, the diffusion coefficient, which is calculated from this portion $(i_p'/V^{1/2})_{V\to\infty}$, taking into account the initial concentration of depolarizer, approaches the literature data.

Thus, extending the range of potential scan rates and making the best use of experimental potentialities of chronovoltammetric method, based on the results of analysis of original data, we can accept more substantiated scheme of the mechanism of Mn^{2+} ions electrooxidation in the acidic medium with subsequent disproportionation of the product of irreversible electrode reaction and hydrolysis. As a result, MnO_2 forms:

$$2Mn^{2+} - 2e \longrightarrow 2Mn^{3+},$$
$$2Mn^{3+} \longrightarrow Mn^{2+} + Mn^{4+},$$
$$\underline{Mn^{4+} + 2H_2O \longrightarrow MnO_2 + 4H^+},$$
$$Mn^{2+} + 2H_2O - 2e \longrightarrow MnO_2 + 4H^+.$$

It should be supposed that, in the acidic medium, the last stage, namely, the formation of manganese dioxide, is the slowest stage. Table 2 lists the calculated parameters of electrode process. Most of them are estimated quantitatively for the first time.

EXPERIMENTAL RESULTS ON THE CATHODIC REDUCTION OF MnO_2 AND DISCUSSION

The cathodic reduction of manganese dioxide is studied also in 0.5 M Na_2SO_4 + 0.1 M H_2SO_4 solution deaerated with argon at a temperature of 298 K. Only one pronounced peak (I) is observed in the voltammograms of MnO_2 electroreduction at relatively low potential scan rates ($V < 0.05$ V/s). At $V > 0.05$ V/s, the

Table 2. Parameters of anodic oxidation of Mn^{2+} on platinum and manganese dioxide electrodes in 0.5 M Na_2SO_4 solution, pH 1, $c = 1 \times 10^{-5}$ mol cm^{-3}

Electrode	χ, cm s^{-1}	δ, cm	D, cm^2 s^{-1}	k_s, cm s^{-1}	k_{bh}^*, cm s^{-1}	ΔG, kJ mol^{-1}	K_{DPP}^{**}, s^{-1}mol^{-1} l
Pt	0.5×10^{-2}	0.5×10^{-2}	3×10^{-6}	9.9×10^{-4}	1.8×10^{-3}	–44.68	3.32×10^2
MnO_2			2.7×10^{-6}	1.54×10^{-3}	4.17×10^{-3}	–17.27	

Notes: * Heterogeneous rate constant of charge transfer at the potential of peak.
** Disproportionation constant of the product of stage: $2Mn^{3+} \longrightarrow Mn^{2+} + Mn^{4+}$.

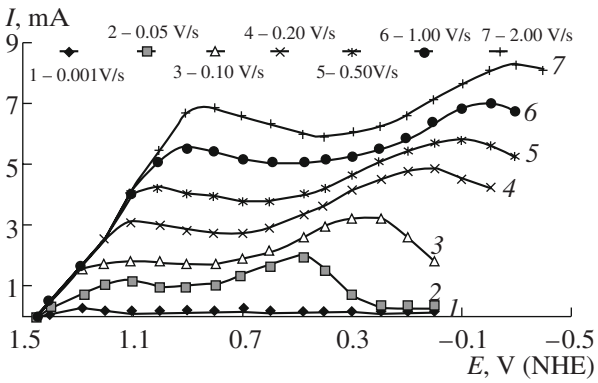

Fig. 9. Voltammograms of MnO_2 electroreduction in 0.5 M Na_2SO_4 solution (pH 1; 298 K).

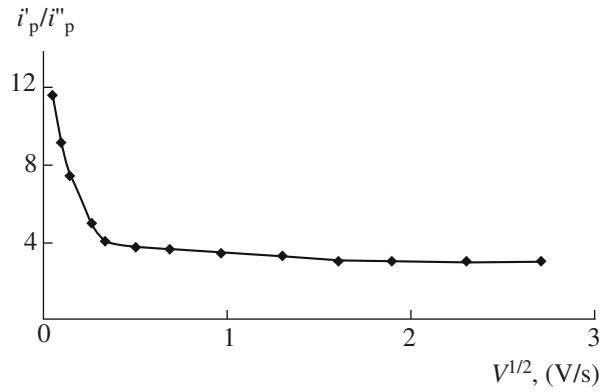

Fig. 10. Plot i'_p / i''_p vs. $V^{1/2}$ for MnO_2 electroreduction in 0.5 M Na_2SO_4 solution (pH 1; 298 K).

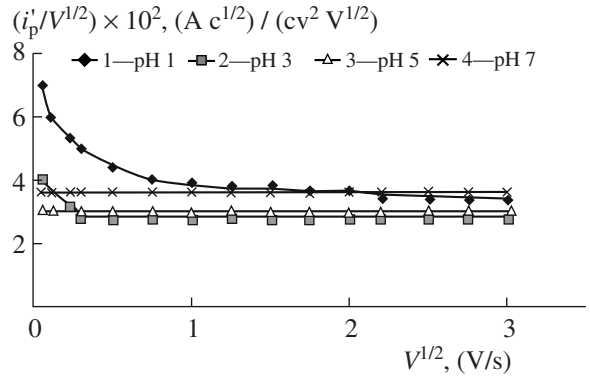

Fig. 11. Plots $i'_p / V^{1/2}$ vs. $V^{1/2}$ for MnO_2 electroreduction in 0.5 M Na_2SO_4 solution (pH1, 298 K).

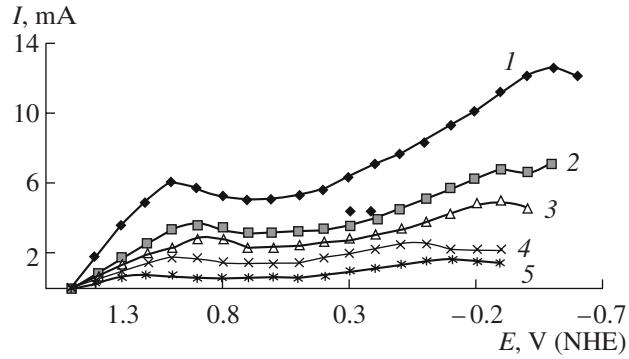

Fig. 12. Voltammograms of MnO_2 electroreduction in 0.5 M Na_2SO_4 solution (pH 1; $V = 2$ V/s) (*1*) after the first pulse, (*2*) after the second pulse with a delay of 3–4 s, (*3*) after the third pulse with a delay of 3–4 s, (*4*) after the 4th pulse with a delay of 3–4 s, (*5*) after the 5th pulse with a delay of 3–4 s.

second peak arises; its height increases with increasing potential scan rate (Fig. 9), whereas the ratio i'/i'' remains almost constant and approximately equal to 3 at $V \geq 0.2$ V/s (Fig. 10). The latter can be due to the capacitance component of polarizing current. With increasing scan rate, the potential of the first peak shifts in the cathodic direction, and the peak width increases. The $i'_p/V^{1/2}$ ratio, first, decreases and, at $V \geq 1$ V/s, becomes almost constant (Fig. 11). A similar plot with slight decreasing $i'_p/V^{1/2}$, ratio is observed also at pH 3, but at smaller scan rates than at pH 1. For the systems with pH 5 and 7, $i'_p/V^{1/2}$ = const throughout the range of potential scan rates. At the scan rates $V \geq 1$ V/s, after several pulses (at 5–6 s intervals), the peaks are suppressed, the first peak decreases by 2–3 times as compared with a similar peak, which was obtained in the previous pulse. The polarization curve stabilizes after several pulses (Fig. 12).

The fact that, under the steady-state polarization conditions, the peaks are observed in the voltammograms, and they become less pronounced with increasing *V*, can be, probably, explained by the coating of the electrode surface with the product of cathodic process. According to the literature data [10], the scheme of electrode reaction can be presented as follows:

$$MnO_2 + e + H^+ \longrightarrow MnOOH. \quad (6)$$

Formed MnOOH, being weakly conducting, partially blocks the electrode surface at small potential scan rates leading to the peak rise. The suppression of the peak after several pulses under high scan rates, probably, can be explained by the formation of MnOOH (Fig. 12). At relatively high cathodic potential scan rates, the chemical reaction of MnOOH formation has no time to realize, and the second wave arises as a result of the second electron transfer to the product of the first stage. Thus, at high potential scan rates, the two-stage electron transfer can be supposed:

$$MnO_2 + e \longrightarrow MnO_2^-, \quad (7)$$

$$MnO_2^- + e + 4H^+ \longrightarrow Mn^{2+} + 2H_2O. \quad (8)$$

Table 3. Parameters of MnO_2 electroreduction in 0.5 M Na_2SO_4 solution (298 K) at various pH values

pH	k_s, cm s^{-1}	k_{bh}, cm s^{-1}	i_0, A cm^{-2}	ΔG, kJ mol^{-1}	E_a, kJ mol^{-1}	D_{H^+}, cm^2 s^{-1}
1	1.02×10^{-8}	7.15×10^{-6}	9.23×10^{-7}	19.5	16.57	3×10^{-5}
3	2.5×10^{-8}	3.5×10^{-6}	2.4×10^{-8}	17.1		
5	8.5×10^{-9}	3.3×10^{-6}	2.0×10^{-10}	3.59		
7	5.5×10^{-10}	1.58×10^{-6}	5.3×10^{-13}	4.15		

Notes: k_s is the standard rate constant of charge transfer; k_{bh} is the rate constant of charge transfer at the peak potential; i_0 is the standard exchange current density; ΔG is the free activation energy of potential-determining stage; D_{H^+} is the diffusion coefficient of H^+ ions.

The shape of $i_p'/V^{1/2}$ vs. $V^{1/2}$ dependence for pH 1–3 points to the presence of conjugate reaction [29]. We may suppose that, in the acidic medium, the product of electrode process is subjected to the disproportionation reaction at the potentials of the first peak, thus supporting the opinion on the presence of catalytic effect [10].

As a result of disproportionation reaction of three-valent manganese compound, MnO_2 deposits on the electrode:

$$2MnO_2 + 2H^+ + 2e \longrightarrow MnOOH, \quad (9)$$

$$2MnOOH + 2H^+ \longrightarrow MnO_2 + Mn^{2+} + 2H_2O, \quad (10)$$

$$MnO_2 + 4H^+ + 2e \longrightarrow Mn^{2+} + 2H_2O. \quad (11)$$

Assuming that the electrode process rate is limited by the rate of diffusion delivery of hydrogen ions to the electrode and substituting their concentration (pH 1, $c_{H^+} = 1 \times 10^{-4}$ mol cm^{-3}) into the equation for the peak current for the non-steady-state processes [29], one can calculate the diffusion coefficient D_{H^+}. The calculation by the relation $(i_p'/V^{1/2})_{V \to 0}$ yields a value of 1.7×10^{-4} cm^2 s^{-1}, which is much higher than the literature data [32, 33]. The calculation of D_{H^+} $(i_p'/V^{1/2})_{V \to \infty}$ (when the process rate is controlled only by the transport limitations) yields a value of the same order (3×10^{-5} cm^2 s^{-1}) as in the above-cited works.

Table 3 lists the kinetic parameters that were calculated by the known criterional dependences of chronovoltammetric method [29]. The activation energy of electroreduction is determined from the data of steady-state measurements using the Arrhenius equation in the temperature range of 298 to 343 K ($i_p^{298} = 3.35 \times 10^{-5}$ A cm^{-2}, $i_p^{343} = 7.2 \times 10^{-3}$ A cm^{-2}).

The shape of E_p vs. $\log V$ curves for various pH values (Fig. 13) indicates that the mechanism of electroreduction for pH 1 changes at a scan rate $V = 0.5$ V/s, which is in agreement with the data presented on Fig. 11. At $V \geq 0.5$ V/s, the conjugate reactions play no important role in the electrode process. The shape of i_p^a vs. $V^{1/2}$ curves (Fig. 14) indicates that the degree of reversibility of cathodic process changes in the test range of potential scan rates.

The fact that the rate of electroreduction is virtually independent of pH value for various potential scan rates

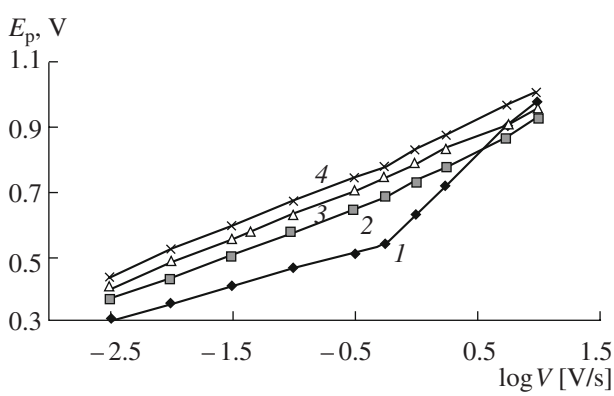

Fig. 13. Plots of E_p vs. $\log V$ for MnO_2 electroreduction in 0.5 M Na_2SO_4 solution (298 K) at pH values: (*1*) 1, (*2*) 3, (*3*) 7, and (*4*) 5.

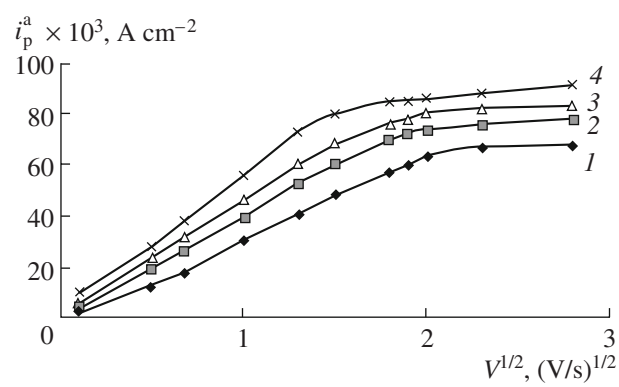

Fig. 14. Plots of i_p^a vs. $V^{1/2}$ for MnO_2 electroreduction in 0.5 M Na_2SO_4 solution (298 K) at pH values: (*1*) 1, (*2*) 3, (*3*) 5, and (*4*) 7.

is the evidence for the complexity of solid-phase reaction mechanism.

The analysis of the voltammograms of solid-phase cathodic process, possibly, is conventional to some extent; however, it enables us to offer a substantiated explanation of peculiarities of the process in agreement with the opinions of other authors on this mechanism.

CONCLUSIONS

The above experimental data and the values of parameters of Mn^{2+} electrooxidation in the acidic medium suggest that the most acceptable scheme is the scheme of anodic formation of manganese dioxide with conjugate chemical reaction: (a) the anodic oxidation of Mn^{2+} with one-electron irreversible transition; (b) the disproportionation of the product of electrode reaction; and (c) the hydrolysis of the product of disproportionation (four-valent manganese) with the formation of MnO_2.

Based on the analysis of experimental data on the MnO_2 electroreduction under the steady-state and non-steady-state potentiodynamic polarization conditions, it is shown that, in the acidic medium (pH 1–3), depending on cathodic potential scan rate, the mechanism of the electrode process changes: at $V < 0.5$ V/s, MnOOH forms as a result of one-electron transition leading to partial deactivation of electrode surface with subsequent disproportionation of MnOOH. At $V > 0.5$ V/s, manganite has no time to form, and two-stage reduction, by an electron at each stage, is well defined.

ACKNOWLEDGMENTS

This work was supported by the Science and Technology Center in Ukraine, project no. GR85.

REFERENCES

1. Mcbreen, J., *Power Sources*, 1975, no. 5, p. 525.
2. Chouacb, F., Cauquil, O., and Lamache, M., *Electrochim. Acta*, 1981, vol. 26, p. 325.
3. Chernysheva, L.S., Efremov, B.N., and Tarasevich, M.R., *Elektrokhimiya*, 1989, vol. 25, p. 844.
4. Reynaud, J., *Bull. Soc. Chim. Fr.*, 1968, p. 47.
5. Sato, M., Matsuki, K., and Sugawara, M., *Kogyo Kagaku Zasshi*, 1968, vol. 71, p. 484.
6. Sato, M., Matsuki, K., and Sugawara, M., *Kogyo Kagaku Zasshi*, 1971, vol. 74, p. 872.
7. Ruetschi, P., Extended Abstracts of Papers, *Electrochem. Soc. Fall Meeting,* Dallas, 1975, p. 17.
8. Lee, J., Maskell, W., and Tye, F., *J. Electroanal. Chem.*, 1977, vol. 79, p. 79.
9. Lee, J., Maskell, W., and Tye, F., *J. Electroanal. Chem.*, 1980, vol. 110, p. 145.
10. Maskell, W., *J. Electroanal. Chem.*, 1986, vol. 198, p. 727.
11. Slaidin', G.A., *Izv. Akad. Nauk. Latv. SSR, Ser. Khim.,* 1980, no. 5, p. 515.
12. Arsdale, G.D. and Maier, C.G., *Trans. Electrochem. Soc.*, 1998, vol. 1, p. 109.
13. Zaretskii, S.A. and Antonovskaya, E.I., in *Elektrokhimiya margantsa* (Electrochemistry of Manganese), Tbilisi, 1967, vol. 3, p. 232.
14. Fleischmann, M., Thirsk, M.R., and Tordevialas, L.M., *Trans. Faraday Soc.*, 1962, vol. 58, no. 9, p. 1865.
15. Reynaud, L.A. and Brenet, L.P., *Bull. Soc. Chim. Fr.*, 1968, no. 9, p. 3505.
16. Sato, M., Macuki, K., and Sugawara, M., *Kogyo Kagaku Zasshi*, 1968, vol. 71, p. 104.
17. Sato, M., Macuki, K., and Sugawara, M., *Kogyo Kagaku Zasshi*, 1969, vol. 72, p. 1073.
18. Sato, M., Macuki, K., and Sugawara, M., *Kogyo Kagaku Zasshi*, 1970, vol. 73, p. 905.
19. Sato, M., Macuki, K., and Sugawara, M., *Kogyo Kagaku Zasshi*, 1972, vol. 75, p. 1838.
20. Vetter, K.J. and Manecke, K.J., *Z. Phys. Chem.*, 1950, vol. 195, p. 377.
21. Sugimori, M. and Sekine, J., *Denru Kagaky*, 1969, vol. 37, no. 1, p. 63.
22. Sugimori, M. and Sekine, J., *Denru Kagaky*, 1969, vol. 37, no. 5, p. 380.
23. Atstinysh, A.Ya., Atstinysh, G.Ya., Slaidin', G.A., and Bagotsky, V.S., *Izv. Akad. Nauk Latv. SSR, Ser. Khim.*, 1978, no. 2, p. 180.
24. Barchese, E., Chages, H.C., and Wolynec, S., *An. Acad. Brasil*, 1981, vol. 53, no. 2, p. 309.
25. Grzegorzewski, A. and Heusler, K.E., *J. Electroanal. Chem.*, 1987, vol. 228, p. 455.
26. Damaskin, B.B., Tsagareli, G.A., and Makhatadze, Sh.M., *Elektrokhimiya*, 1988, vol. 24, p. 1123.
27. Mdivani, M., Gogoladze, P., and Agladze, T., Abstracts of Papers, *The First Agladze Symposium on Electrochemistry of Manganese*, Tbilisi, 1991, p. 15.
28. Galus, Z., *Teoretyczne podstawy electroanalizy chemicznej*, Warszawa: Panstwowe Wydawnictwo Naukowe, 1971.
29. Gorokhovskaya, V.I. and Gorokhovskii, V.M., *Praktikum po ostsillograficheskoi polyarografii* (Practical Course on Oscillographic Polarography), Moscow: Vysshaya Shkola, 1973.
30. Budnikov, G.K., *Printsipy i primenenie vol'tampernoi ostsillograficheskoi polyarografii* (Principles and Application of Voltammetric Oscillographic Polarography), Kazan: Kazan Gos. Univ, 1975.
31. Eggins, B.R., *Faraday Discuss. Chem. Soc.*, 1973, vol. 56, p. 276.
32. Kvaratskheliya, R.K. and Kvaratskheliya, E.R., *Elektrokhimiya*, 1999, vol. 35, p. 537 [*Russ. J. Electrochem.* (Engl. Transl.), vol. 35, p. 490].
33. Vielstich, W. and Jahn, D.J., *Advances in Polarography. Langmuir*, Oxford: Pergamon, 1960, p. 281.

View publication stats