

# Research Journal of Pharmaceutical, Biological and Chemical Sciences

## Chemical and Electrochemical Behavior of Manganese Dioxide Film in Various Solutions.

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### ABSTRACT

The thin film of manganese dioxide (MD) was electrochemically deposited on the surface of platinum in solutions which did not contain manganese  $Mn^{2+}$  ions and on the voltammetric curves was observed the current peak in the potentials of electrochemical oxidation of  $Mn^{2+}$  ions to  $MnO_2$ . Due to the anodic polarization at the corresponding potential, the current fell to background values. Afterwards, Pt/ $MnO_2$  electrode was kept in solution containing  $Mn^{2+}$  ions and then recorded voltammogram in  $Na_2SO_4$  reproduced the original curve during the anode sweep of the potential. These results indicate a superficial nature of the studied effects and can be explained by the chemisorption of  $Mn^{2+}$  ions on the MD surface. Chemisorption leads to the formation of Mn (III) particles, which then can be electrochemically oxidized to MD. In a solution of only manganese sulfate or sulfuric acid, the MD film did not dissolve; however, when they were combined in the solution, it was chemically dissolved. This process was studied by the method of Rotating Ring-Disk Electrode (RRDE). Apparently, the first stage of dissolution of MD is the chemisorption of  $Mn^{2+}$  ions with the formation of Mn (III) particles on the MD surface. Further, chemical dissolution of the formed particle in sulfuric acid takes place.

**Keywords:** Manganese Dioxide, electrodeposition, chemisorption, film, voltammetry, reaction mechanism.

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## INTRODUCTION

Manganese Dioxide (MD) is used as an oxidizer of some organic [1, 2] and inorganic compounds (for example, oxidation of CO to CO<sub>2</sub>) [3], also as an alternative of the platinum catalyst in the reduction of oxygen [4, 5], as well as a sorbent and catalyst [6,7]. However, the major world production is consumed in manufacture the world's most common chemical current sources [8, 9]. In recent time, MD is considered as an affordable and cheap material for creating electrochemical capacitors [10-12]. There are many ways of forming the manganese dioxide electrodes for electrochemical supercapacitors [13, 14]. Anodic deposition of a thin MD film has a number of advantages. This method allows to control the thickness of the film, the deposit on the substrate is homogeneous without using a binder and carbon material, as in the case of powders. The MD film with desired properties can be obtained by changing the conditions of electrodeposition [13, 14].

Electrodeposition of MD from solutions containing manganese ions Mn<sup>2+</sup> is a complex reaction with a number of chemical and electrochemical stages [15, 16]. Until now, this issue remains the subject of discussions. The reaction mechanism depends strongly on the reaction conditions, such as, solution composition, temperature and current density. Often this explains the apparent contradictions.

The aim of the work is to elucidate the mechanism of the reaction of electrodeposition of MD and the role of chemisorption in the formation of intermediate particles.

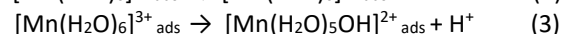
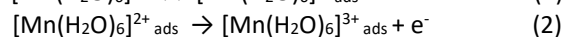
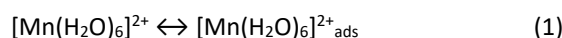
The use of an electrode from thin DM films in supercapacitors is based on a rapidly proceeding reversible redox reaction with a change in the degrees of oxidation, Mn<sup>3+</sup> and Mn<sup>4+</sup>. The film must withstand a large number of charge-discharge cycles and have mechanical and chemical resistance. Therefore, the study of the behavior of the MD film in electrolyte solutions is of great interest.

On the basis of the literature data in [17], three main mechanisms of electrodeposition of MD are considered, which depend on the experimental conditions. It is generally accepted that electrochemical oxidation of Mn<sup>2+</sup> to Mn<sup>3+</sup> occurs at the first stage. Then, in weakly acidic solutions, hydrolysis proceeds with the formation of MnOOH precipitate on the electrode and further, solid-phase oxidation of MnOOH to MnO<sub>2</sub>.

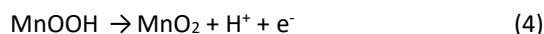
The second mechanism assumes the loss of the second electron, formed in the first stage by the Mn<sup>3+</sup> ion, and forming Mn<sup>4+</sup> particle, which rapidly undergoes hydrolysis and is converted into MnO<sub>2</sub>.

At high acidity, a third mechanism is realized. Under these conditions, the Mn<sup>3+</sup> ion is more stable, it manages to disproportionate and the resulting Mn<sup>4+</sup> is converted to MnO<sub>2</sub>, as in the second case [17].

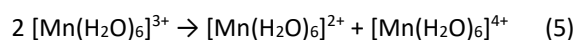
Clark and co-workers [18] studied the mechanism of electrodeposition of MD in solutions with different concentrations of MnSO<sub>4</sub> and H<sub>2</sub>SO<sub>4</sub> by the rotating-disc electrode (RDE) method and proposed two mechanisms of electrochemical oxidation of the Mn<sup>2+</sup> ion. In dilute solutions of H<sub>2</sub>SO<sub>4</sub> (< 1.0 M):



Further,  $[\text{Mn}(\text{H}_2\text{O})_5\text{OH}]^{2+}_{\text{ads}}$  is rapidly converted to MnOOH, which is electrochemically oxidized to MnO<sub>2</sub> by reaction:



In concentrated solutions of H<sub>2</sub>SO<sub>4</sub> (>1.0 M), the formed  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$  ion at the first stage passes into the solution where disproportionation takes place:



The formed  $[\text{Mn}(\text{H}_2\text{O})_6]^{4+}$  ion is rapidly hydrolyzed to MnO<sub>2</sub> [18].

## MATERIALS AND METHODS

Chemical and electrochemical behaviors of MD films were investigated in standard three-electrode cell with separated cathodic and anodic spaces. The chemisorption of  $Mn^{2+}$  ions on the MD surface was studied on a platinum rotating disk electrode (RDE) with a 1 mm diameter. For studying dissolution, a rotating ring-disk electrode (RRDE) was used. The radius of the disk was 0.25 cm; the inner radius of the ring was 0.275 cm; the outer radius of the ring was 0.359 cm; the efficiency factor of the RRDE with such a geometry is  $N=0.4$ , in other words, 40% of the product, obtained on the disk, due to the centrifugal forces, reaches the ring. A MD film was deposited on the surface of the disk electrode. Chemical dissolution was performed with an open circuit of the disk electrode, whereas for fixing the dissolution product, the  $Mn^{3+}$  ions on the ring electrode were set to a potential of 0.08 V.

The auxiliary electrode was a platinum plate; the reference electrode was a mercury sulfate electrode in 0.5 M  $H_2SO_4$ . The surface of the platinum electrode was polished with finely ground glass powder, and then washed with hot water, benzene, alcohol and again with water. Prior to the measurements, the electrode was periodically subjected to anodic-cathodic polarization in the range of potentials from the evolution of oxygen to hydrogen evolution in 0.5 M  $H_2SO_4$ .

Twice distilled water was used to prepare the working solutions. The salts reagents were additionally purified by recrystallization, sulfuric acid was twice distilled.

Preliminary deposition of MD on the surface of the disk electrode was carried out at 25°C from neutral ( $0.4 \text{ M Na}_2\text{SO}_4 + 2 \cdot 10^{-2} \text{ M Mn}^{2+}$ ) and acidic ( $0.2 \text{ M Na}_2\text{SO}_4 + 0.2 \text{ M H}_2\text{SO}_4 + 2 \cdot 10^{-2} \text{ M Mn}^{2+}$ ) solutions in coulometric mode at a constant potential: 0.6 V for neutral solution and 0.8 V for acidic solution. In acidic solutions part of the intermediate particles of the  $Mn^{3+}$  reaction passed into the solution. Thus, the current efficiency of the MD was less than 100%. To calculate the mass of MD, and hence the thickness of the film, was chosen a solution in which the MD film was electrochemically completely dissolved and the mass of MD was found via the amount of electricity used for its dissolution. The obtained data was compared with the amount of electricity consumed by the electrodeposition of the film. The current efficiency of MD in neutral solutions was almost 100% and in acidic solutions it was 94%. The density of MD was taken as  $4.2 \text{ g/cm}^2$ . The thickness of the films was about 200 nm (if it is not specified in the text). The measurements were carried out at 25°C on the universal polarograph GWP-673 and on the potentiostat PalmSens4.

## RESULTS AND DISCUSSION

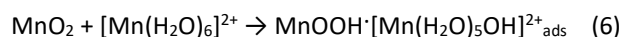
### CHEMISORPTION OF MANGANESE IONS (II) ON THE MANGANESE DIOXIDE SURFACE

In 0.4 M  $Na_2SO_4$ , the current peak in the region of the potentials of the electrochemical oxidation of  $Mn^{2+}$  was observed on the Pt/ $MnO_2$  electrode when the potential was swept to the anodic direction (Fig. 1). In paper [19] this behavior of MD was associated with its non-stoichiometry. The observed anodic currents are explained by the solid-phase electrochemical oxidation of  $MnO_x$  (the index  $x$  is always less than 2). In this paper it was assumed that an oxidized compound in a solid phase with a low degree of oxidation of manganese is  $MnOOH$ . When it is oxidized to  $MnO_2$ , a proton must be released. A slow stage is the diffusion of  $H^+$  ions in the solid phase [19]. In the anodic polarization of MD, the degree of oxidation of manganese actually increases, however, this occurs as a result of the polarization of the electrode for several days and the current associated with the solid-state oxidation of  $MnO_x$  is negligible [20].

In our experiments, the current at the maximum point of the curve obtained at the anodic scanning of the potential in the 0.4 M  $Na_2SO_4$  (with no manganese ions) could exceed the value of the limited electrodeposition current of MD in a solution of 0.4 M  $Na_2SO_4 + 2 \cdot 10^{-2} \text{ M MnSO}_4$ . As can be seen from Fig.1, the current is rapidly decreased, practically to the background value, and at the repeated curve the anodic peak was no longer observed (Fig. 1, curve 2). If the freshly deposited MD film was polarized at a potential of 0.55 V in a solution of  $Na_2SO_4$ , the current was rapidly dropped almost to zero. After that, the MD film was kept in a solution of  $10^{-3} \text{ M MnSO}_4$ , then the electrode was thoroughly washed with water and the voltammetric curve was recorded in a  $Na_2SO_4$  solution. The results are shown in Fig. 2, curve 1. As it can be observed, the voltammogram reproduced the original curve of Fig. 1. An analogous voltammogram was obtained in the case of preliminary keeping of the MD film in a solution of 0.2 M  $Na_2SO_4 + 10^{-3} \text{ M MnSO}_4$ , Fig.

2, curve 2. When Na<sub>2</sub>SO<sub>4</sub> was replaced by H<sub>2</sub>SO<sub>4</sub>, the anodic peak was decreased significantly, Fig. 2, curve 3. Curves 4-6 in Fig. 2 were obtained in the same conditions. For the curves 1-3, MD films were formed in neutral solution and the rest curves, 4-8, were recorded on MD film, formed in acidic solution. The curve 7 was obtained after holding the Pt/MnO<sub>2</sub> electrode in Mn<sup>2+</sup> solution and subsequent anodic polarization, and the curve 8 - after keeping only in H<sub>2</sub>SO<sub>4</sub> solution (without anodic polarization).

These results prove the superficial nature of the studied effects. Such a high value of the current value after exposure of MD in MnSO<sub>4</sub> solution is well explained by the chemisorption of Mn<sup>2+</sup> ions on the MD surface, which can be represented by the equation:



Wells et al. [21] investigated the hydrolysis of hexa aqua Mn (III) ions and showed that the equilibrium constant of the first stage of hydrolysis is  $K = 0.88$ . Thus, even in sufficiently acidic solutions,  $[\text{Mn}(\text{H}_2\text{O})_5\text{OH}]^{2+}$  ions are formed in the significant amount. Clark and co-workers also noted the easiness of hydrolysis of  $[\text{Mn}(\text{H}_2\text{O})_6]^{3+}$ ,  $\text{pK}_a = 0.03$ , and on this base justified the existence of an adsorbed  $[\text{Mn}(\text{H}_2\text{O})_5\text{OH}]^{2+}_{\text{ads}}$  particle on the MD surface. However, unlike our conclusions, the authors believe that Mn(III) is formed as a result of electrochemical oxidation of Mn(II), equation (2) [18].

Thus, the chemisorbed particles were dissolved in H<sub>2</sub>SO<sub>4</sub> and passed into solution as Mn (III) ions, which will be discussed in more detail below.

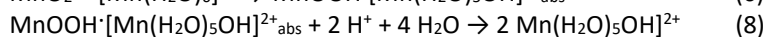
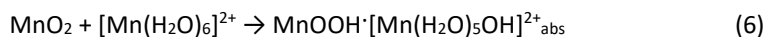
In the case of anodic polarization of Pt/MnO<sub>2</sub> electrode, the chemisorbed Mn (III) electrochemically was oxidized to MnO<sub>2</sub>.



The area under the current-voltage curves corresponds to the amount of electricity expended on the oxidation of chemisorbed particles. Increasing of the concentration of Mn<sup>2+</sup> ions in the solution with the preliminary keeping of the Pt/MnO<sub>2</sub> electrode, initially led to an increase of the amount of electricity utilized on the oxidation of chemisorbed particles, but then it was not changed, which indicates the limited filling of the MD surface with chemisorbed particles, Fig.3. Thus, it is possible to calculate the chemisorption of Mn<sup>2+</sup> ions on the MD surface. Using a series of voltammograms obtained after keeping the MD film in solutions with different concentrations of MnSO<sub>4</sub>, an isotherm of adsorption was constructed (Fig. 3). The step in upper part of the curve is difficult to interpret, probably, it is associated with the heterogeneity of the MD pores. Taking into account that on the oxidation of chemisorbed particles accounted the half of the consumed amount of electricity, the value of the limited adsorption per unit area of the visible surface was calculated. It turned out to be equal to  $9 \cdot 10^{-8}$  mol/cm<sup>2</sup>. This value seems quite reasonable, considering that the porosity of the electrodeposited MD can reach 30-50 m<sup>2</sup>/g and the mass of the precipitated MD in our case was  $6.96 \cdot 10^{-7}$  g.

#### CHEMICAL DISSOLUTION OF MANGANESE DIOXIDE FILM

In solutions containing only H<sub>2</sub>SO<sub>4</sub> or MnSO<sub>4</sub> separately, the MD film previously deposited on the disk surface was not dissolved and no cathodic reduction current of Mn<sup>3+</sup> ions was observed at the ring electrode. However, when the solution contained both H<sub>2</sub>SO<sub>4</sub> and MnSO<sub>4</sub>, MD was dissolved and the cathodic reduction current of Mn (III) ions was appeared on the ring. The chemical interaction of Mn (II) ions with MD, leading to the formation of MnOOH, is described in a number of papers, which write about the electrochemical oxidation of Mn (II) ions and the reduction of MD [15, 22]. At relatively low concentrations of Mn<sup>2+</sup> ions in the solution, the value of cathodic current at the ring, and consequently, the rate of dissolution of the MD, was increased proportionally with increasing the concentration of Mn<sup>2+</sup> ions. However, with its further increase, the cathodic current on the ring became less and less dependent on their ion concentration, tending to the limit. This behavior can be considered as another proof of the chemisorption of Mn<sup>2+</sup> ions on the MD surface. When the limited surface coverage of chemisorbed particles is reached, an increase in the concentration of Mn<sup>2+</sup> ions in the volume of the solution should no longer effect on the dissolution rate of MD, which was observed experimentally in Fig.4. Thus, dissolution of MD proceeds in two stages:



The total equation has the form

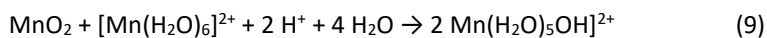


Figure 5 shows the dependence of the cathodic current of reduction of  $\text{Mn}^{3+}$  ions on the ring on the concentration of  $\text{H}_2\text{SO}_4$  in logarithmic coordinates. As can be seen, this dependence practically is linear over the entire range of concentrations studied. The order of the reaction, calculated from the tangent of the slope of the line, turned out to be close to the one, which corresponds to the first order by  $\text{H}_2\text{SO}_4$  and agrees with the equation (8).

For calculation of the rate of chemical dissolution of MD, the following equation can be used:

$$V = \frac{1,25 i}{nFS}$$

Where  $i$  – current on the ring;  $n$  – the number of electrons used on the formed particle;  $F$  – the Faraday constant;  $S$  - the area of the disk. The theory of RRDE is developed for electrochemical processes, proceeding on the disk electrode and in the case when the ring reaches 40% of the formed particles on the disk, the numerical coefficient should be equal to 2.5. However, in our case, the reducing agent is not the electrode, but the  $\text{Mn}^{2+}$  ions from the solution, equation (1). Thus, half of the  $\text{Mn}^{3+}$  ions reaching the ring come from the solution, therefore the numerical coefficient is half as much as the usual value and is equal to 1.25.

The increase in temperature led to the reduction of the dissolution time of the MD film, i.e. to an increase of its dissolution average rate. In this case, the magnitude of the current on the ring and the amount of consumed electricity decreases (fig. 6). This contradiction can be explained by the instability of  $\text{Mn}^{3+}$  ions with increasing of temperature. From the slope of the graph of the dependence of the dissolution rate of MD on temperature, the activation energy of the MD dissolution process was determined, which turned out to be 25 kJ/mol. From the Figure (7) can be seen that amperage on the ring depends on rotation rate of the ring but deviates from the straightness at the higher electrode rotation rates. According to these results, the rate of chemical dissolution of MD is mainly determined by diffusion. Increasing the thickness of the film greatly increases the dissolution rate of Manganese Dioxide. MD is a porous substance, so increasing its mass leads to an increase in the true surface. It follows that the rate of dissolution of MD is controlled by the diffusion of  $\text{Mn}^{3+}$  ions into the bulk of the solution. The diffusion of other particles, participating in the reaction,  $\text{Mn}^{2+}$  or  $\text{H}^+$  ions, should depend only on the geometric area of the disk electrode, and not on its true surface, i.e. mass of the electrode.

It should be mentioned that similar results were obtained when  $\text{Fe}^{2+}$  ions were added to the  $\text{H}_2\text{SO}_4$  solution. In this case, the dissolution of MD was occurred at a higher rate.

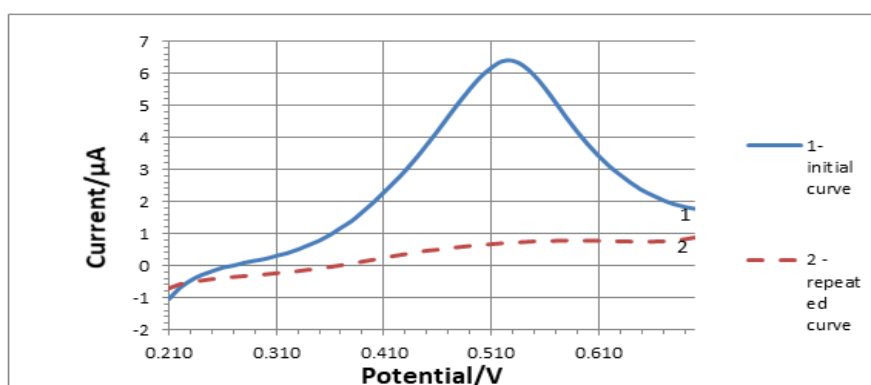


Fig.1. Voltammetric curves on a Pt/ $\text{MnO}_2$  electrode in a solution of 0.4 M  $\text{Na}_2\text{SO}_4$ ;  $\omega = 250$  rpm,  $V = 0.6$  V / min. 1 - initial curve; 2 - repeated curve.

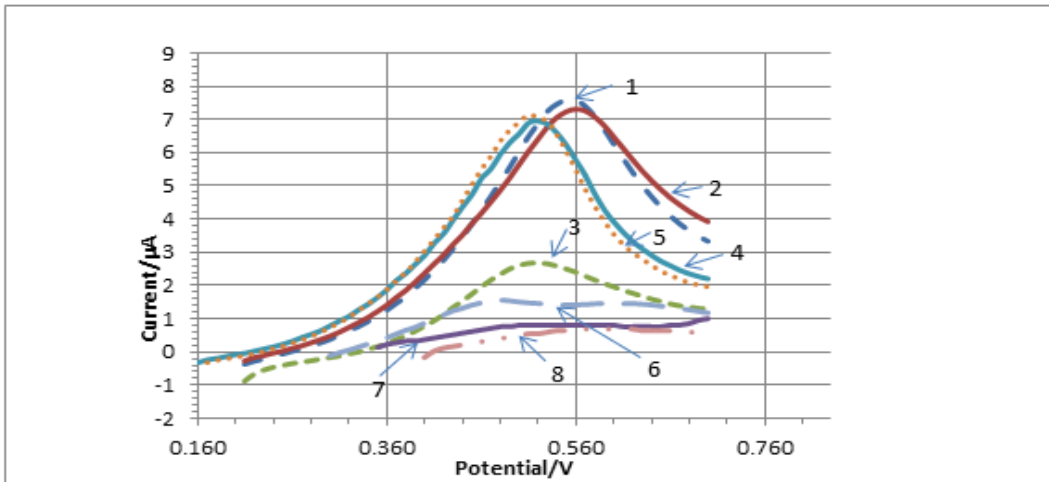
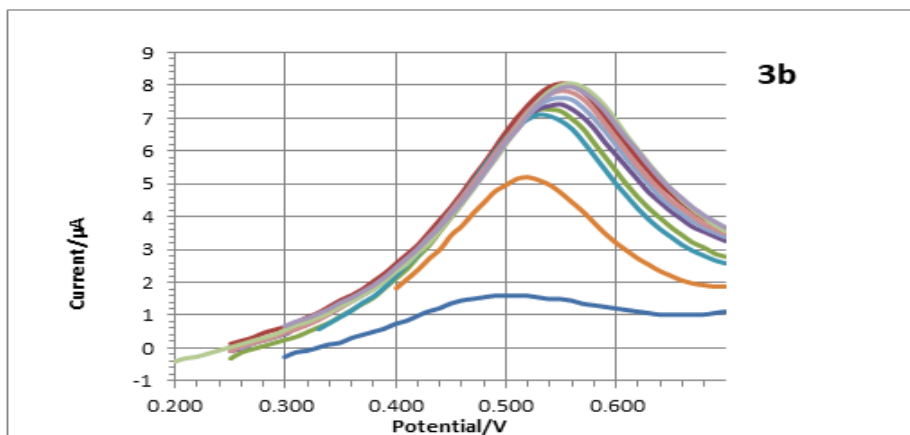
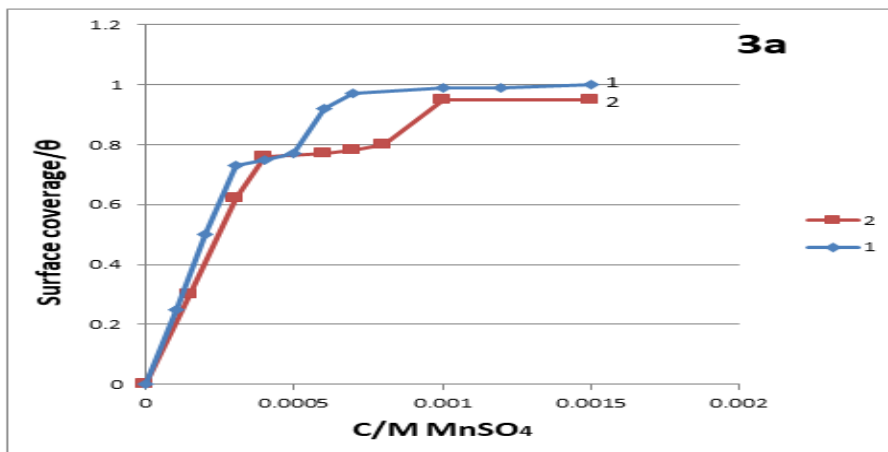


Fig. 2. Voltammetric curves on the Pt/MnO<sub>2</sub> electrode in a solution of 0.4 M Na<sub>2</sub>SO<sub>4</sub>;  $\omega = 250$  rpm,  $V = 0.6$  V / min.

MD film was formed in neutral solution, polarized anodically at 0.6 V in Na<sub>2</sub>SO<sub>4</sub> and then was keeping in: 1 - 10<sup>-3</sup> M MnSO<sub>4</sub>; 2 - 10<sup>-3</sup> M MnSO<sub>4</sub>+0.2 M Na<sub>2</sub>SO<sub>4</sub>; 3 - 10<sup>-3</sup> M MnSO<sub>4</sub>+0.2 M H<sub>2</sub>SO<sub>4</sub>;

MD film was formed in acidic solution, polarized anodically at 0.6 V in Na<sub>2</sub>SO<sub>4</sub> and then was keeping in: 4 - 10<sup>-3</sup> M MnSO<sub>4</sub>; 5 - 10<sup>-3</sup> M MnSO<sub>4</sub>+0.2 M Na<sub>2</sub>SO<sub>4</sub>; 6 - 10<sup>-3</sup> M MnSO<sub>4</sub>+0.2 M H<sub>2</sub>SO<sub>4</sub>;

7 - MD film was previously polarized at 0.6 V; 8 - MD film was previously kept in 0.2 M H<sub>2</sub>SO<sub>4</sub>;



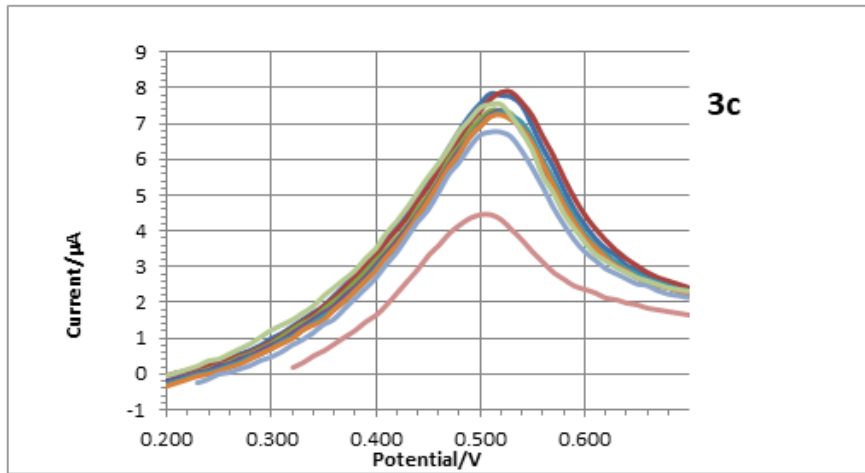


Fig. 3. Dependence of surface coverage of the MD by chemisorbed particles on the concentration of Mn (II) ions in the solution used for preliminary soak of Pt/MnO<sub>2</sub> electrode. 3a – Adsorption isotherm: 1-films obtained in neutral solution (voltammograms 3b); 2-films obtained in acidic solution (voltammograms 3c).

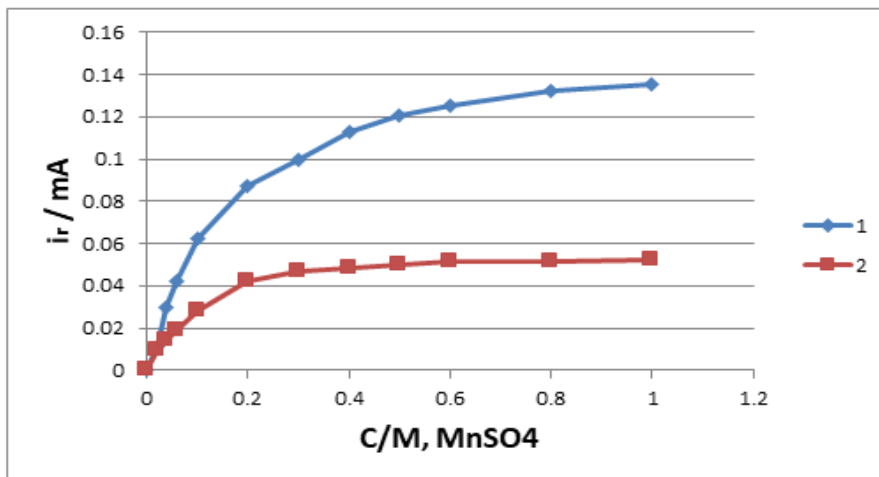


Fig. 4: Dependence of the ring current on the concentration of MnSO<sub>4</sub> during the chemical dissolution of MnO<sub>2</sub>;  $\omega = 650$  rpm, in solution: 1 - 1 M H<sub>2</sub>SO<sub>4</sub>, 2 - 2 M H<sub>2</sub>SO<sub>4</sub>.

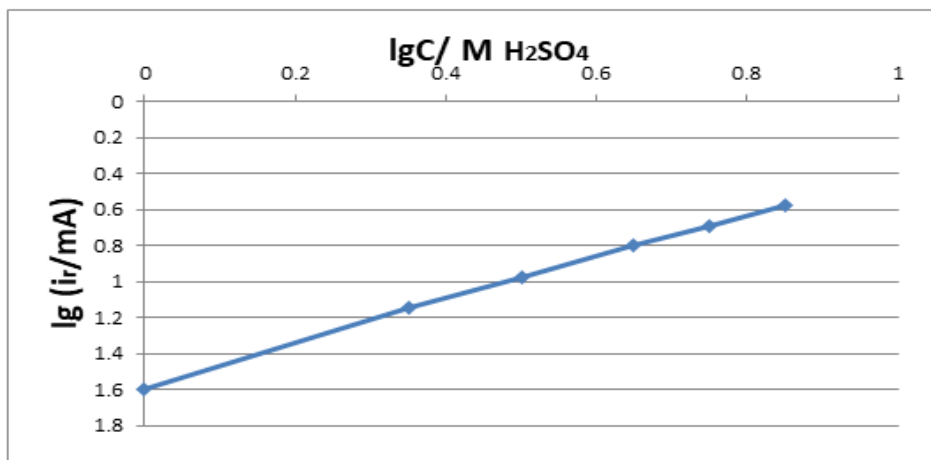


Fig. 5: Dependence of the ring current on the concentration of H<sub>2</sub>SO<sub>4</sub> during the chemical dissolution of MnO<sub>2</sub>;  $\omega = 650$  rpm, 25 °, 0.1 M MnSO<sub>4</sub>,



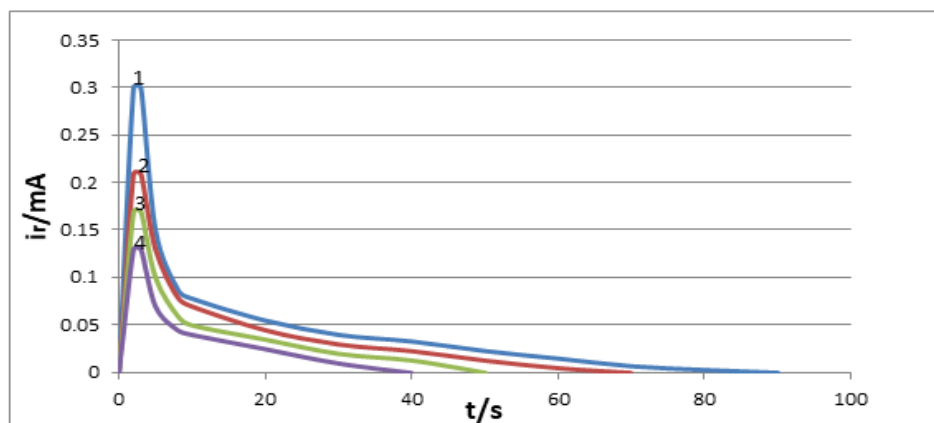


Fig.6: Chronoammograms on the ring during chemical dissolution of  $\text{MnO}_2$  in solution: 0.5 M  $\text{MnSO}_4$  + 2 M  $\text{H}_2\text{SO}_4$ ,  $\omega = 280$  rpm, film thickness 50 nm; temperature: 1 - 20°C; 2 – 30°C; 3 – 40°C; 4 – 50°C.

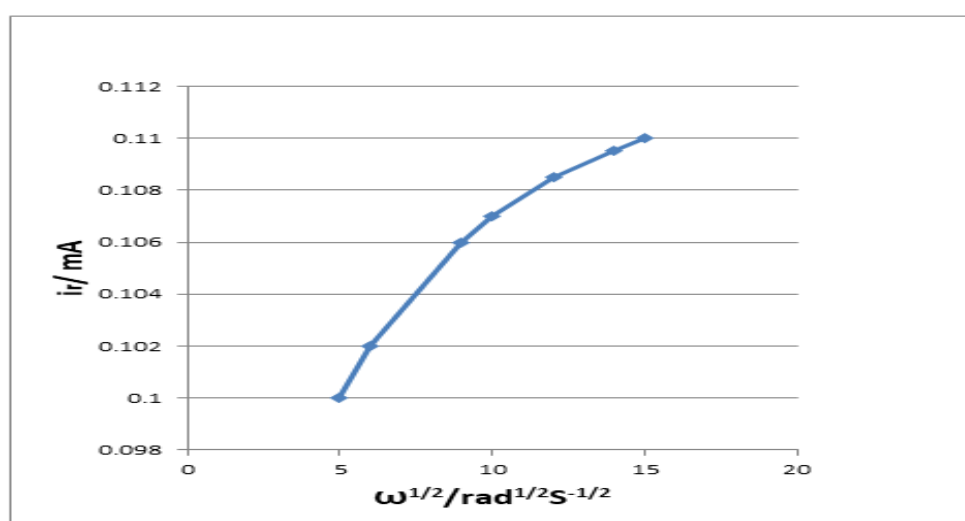


Fig.7: Dependence of  $i-\sqrt{\omega}$  on the ring electrode during chemical dissolution of  $\text{MnO}_2$ .

### CONCLUSION

In solutions, containing Mn (II) ions, occurs chemisorption of these ions on the surface of MD to form Mn (III) particles. The chemisorbed Mn (III) particle is capable of electrochemically oxidation to  $\text{MnO}_2$ . Apparently, the electrodeposition of the MD takes place in two stages: initially, chemically sorbed Mn (III) particles are generated on the surface of growing MD and then their electrochemical oxidation to  $\text{MnO}_2$  occurs.

MD is chemically soluble in solutions containing  $\text{H}_2\text{SO}_4$  and Mn (II) ions. This process also takes place in two stages: at the first stage the chemisorbed Mn (III) particles are produced, and at the second stage - their transition into solution under influence of  $\text{H}_2\text{SO}_4$  occurs. In general, the rate of the process is controlled by the diffusion of the Mn (III) ion into the bulk of the solution.

### ACKNOWLEDGMENT

The work was carried out with the financial support of the Shota Rustaveli National Science Foundation of Georgia within the framework of the Fundamental grant № FR17\_478.



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