# Kinetic of Manganese Electrodeposition Reaction

*Tamaz Agladze, Maia Gabrichidze,Marina Mdivani*

Kinetics of manganese deposition reaction was studied on the basis of analysis of partial rates of manganese discharge and hydrogen evolution reactions measured in a wide range of potentials in a mixture of manganese and ammonium sulphates.

It was shown that fast discharge of manganese ions is followed by rapid chemical interaction of surface atoms with solvent molecules yielding hydrogen gas and oxidized surface layer which further dissolves slowly as a result of chemical interaction with ammonium ions.

Overall kinetic parameters of manganese electrodeposition process are determined by the ratio of rates of surface oxidation/activation reactions. With an increase in overvoltage unfavorable ratio of these rates leads to kinetic limitations of deposition reaction. The proposed reaction model accounts for a number of peculiarities, such as independence of dissolution rate of manganese from potential under cathodic polarization and catalysis of hydrogen evolution reaction proceeding with current yield higher than 100%.

For more information, contact:
Prof. Tamaz Agladze
Department of Electrochemical Engineering
Georgian Technical University
Kostava 77, Tbilisi 380075
Georgia

Phone/Fax: +995 32 334813
E-mail: georgeng@ip.osgf.ge

## Introduction

Manganese metal is traditionally used in metallurgy of steel and non-ferrous alloys. The purest form of this metal is produced on industrial scale by extraction electrolysis from aqueous sulphate solution[1,2]. Recently it was found that Mn-Zn and manganese composite coatings exhibit high corrosion resistance [3-5].

## Experimental

Current yield (CY) and partial rates (PR) of manganese electrodeposition were determined from mass change of cathode (0.6 cm$^2$ PT) at constant potentials. In some experiments volume of hydrogen gas evolved at cathode was also registered. Prior to polarization substrate of cathode was etched in sulfuric acid, degreased by soda and washed by double distilled water. To avoid variation in time of the composition of the electrolyte and to control mass-transfer conditions experiments were conducted in a cell with separate anodic and cathodic apartments under stirring conditions. Part of experiments was carried out at rotating manganese disk electrode. SEM photos of manganese deposits obtained after 30-60 min of cathodic polarization were used to analyze structure of electrodeposits at different potentials. Allotropic modification of manganese was also examined on the basis of X-Ray diffraction patterns of manganese deposits.

It is noteworthy that deposition rates and shape of partial cathodic curves of manganese significantly vary with purity of the electrolyte (Fig.1). In purified electrolytes deposition rates at low overvoltages are about one order of magnitude higher than in unpurified ones. Differences in deposition rates decrease with an increase in overvoltage. Addition of $Na_2SeO_4$ results in elimination of the effect of impurities, especially at high cathodic current densities.
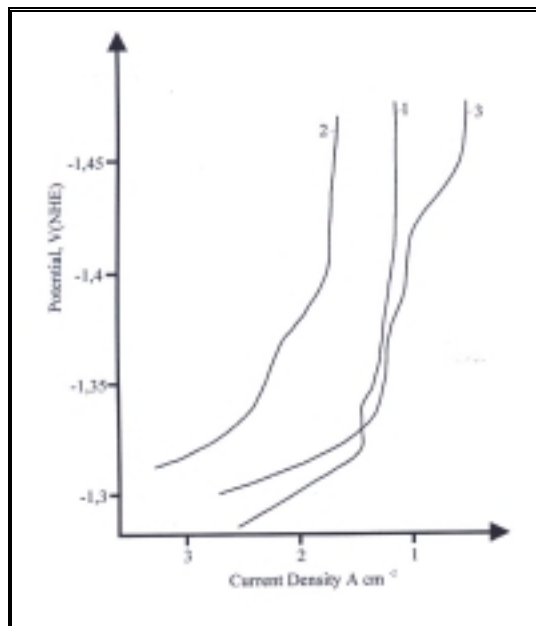


Fig. 1 – Effect of solution treatment and addition of $Na_2SeO_4$ on Mn Deposition rate in 70g.l.$^{-1}$ $(NH_4)_2SO_4$ + 110 g.l.$^{-1}$ $MnSO_4$
1. Prepared from double recrystallized salts.
2. Prepared from reagent grade chemicals
3. The same as in 2, but with addition of 0,21 g.l$^{-1}$ $Na_2SeO_4$

Kinetic measurements were conducted in electrolytes, prepared from double crystallized reagents and subjected to purification by electrolysis at cathodic current density $10^{-4}$ A cm$^{-2}$ during 20 hours. After such treatment bright manganese deposits at platinum and aluminum were obtained with CY up to 90% even at elevated temperatures.

Dissolution rates of manganese under cathodic polarization were calculated from analytical measurements of the amount of metal ions in the solution by means of photocolourimetric or atomic absorption spectrometric analysis [9-10].

## Current Yield

Variation of CY with potential is shown in Fig.2. At platinum substrate maximum CY (• 80%) is reached at potentials  - 1,52-1,54 V decreasing to 30% with an increase in cathodic polarization. At potentials negative to – 1,68 V CY is almost insensitive to changes in potential. Similar behavior was found at titanium and stainless steel substrates. At concentration of

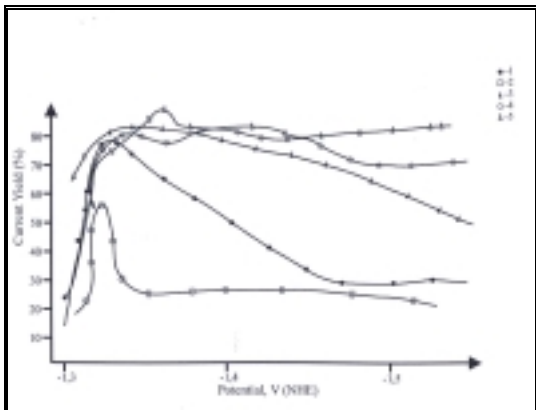NaSeO$_4$ higher than 0,21 g l$^{-1}$ current yield becomes less sensitive to changes in overvoltage.



Fig. 2 – Variation of current yield of Mn with potential in 150 g. l$^{-1}$ (NH$_4$)$_2$SO$_4$ + 110 g.l$^{-1}$ MnSO$_4$ + X g.l.$^{-1}$ Na$_2$SeO$_4$; X: 1 – 0,0; 2 – 0,0105;
3- 0,105; 4 – 0,21; 5 – 0,525

## Partial Curves
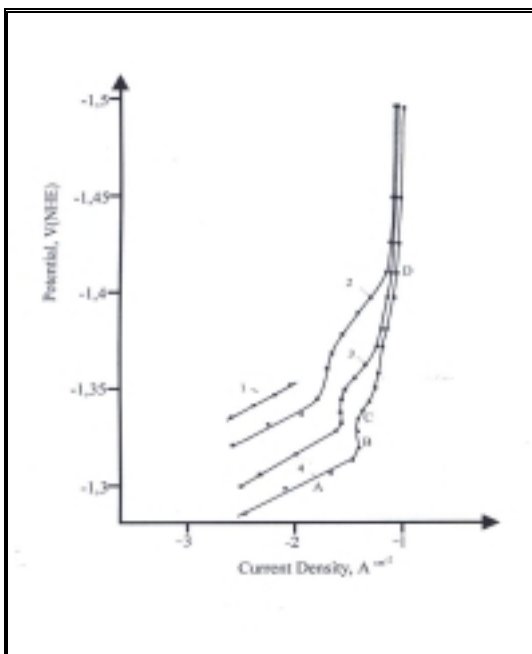


Figure 3 – Partial deposition curves of Mn at various concentrations of MnSO$_4$ in 70 g.l$^{-1}$ (NH$_4$)$_2$ SO$_4$ + X g.l.$^{-1}$ Mn (II), X, g.l$^{-1}$: 1 – 9,06; 2 –27,2; 3 – 82,4; 4 – 110.

Semi-logarithmic partial rates of manganese electrodeposition reaction are given in Fig.3. At low overvoltages partial curves follow Tafel relationship (region - A).

The slope of linear part is close to 2,3 RT/2F and does not change significantly with the variation in manganese and ammonium ions concentration and pH of the electrolyte. In Tafel region deposition rate is independent of pH and increases with a rise in manganese ion concentration. The reaction order ($\cdot$ lgi/$\cdot$ lgc$_{Mn(II)}$)$_E$ calculated from the slope of linear dependence (1) shown in Fig.4 is close to 1,6.

The rate equation for manganese deposition reaction in Tafel region can be described as follows:

$$i_1 = k_1(C_{Mn(II)})^{1.6} \exp(-2 FE/RT), \quad (1)$$

In the region of medium overvoltages (region - C) second cathodic branch, where deposition rate increases with a rise in overvoltage, is observed. This branch is separated from Tafel region by a region of first limiting current (region – B).
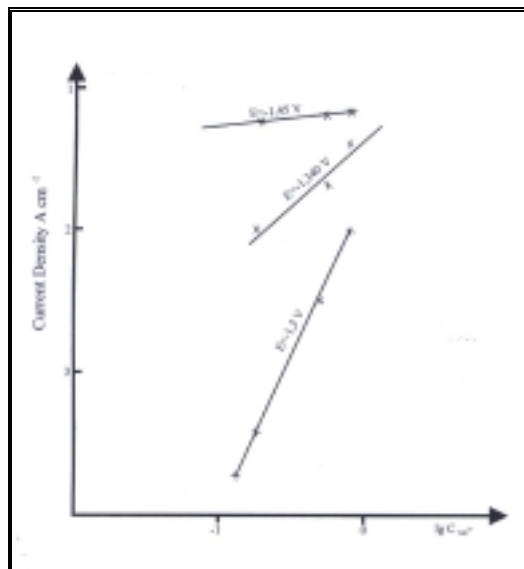


Fig. 4 – Dependence of Mn deposition rate on concentration of Mn(II) ions (g.l $^{-1}$) in 70g.l$^{-1}$ (NH$_4$)$_2$ SO$_4$

At high overvoltages the second limiting current is observed (region – D). Contrary to the first one, deposition rate in this region is almost independent of the concentration of manganese ions in the electrolyte (Fig.4). It is important to mention that in the whole region of potentials the deposition rate of manganese is insensitive to the rotation rate of manganese disc electrode indicating the kinetic nature of limitations of the deposition rate.

## Dissolution of Manganese

At the earliest stage of investigation of the kinetics of manganese electrode it was noted that due to high chemical reactivity manganese dissolves at high rates even under cathodic polarization, affecting significantly Mn deposition reaction [6, 9,10].

Dissolution reaction of manganese under cathodic polarization exhibits a number of peculiarities. At corrosion potential ($E_c$) and a bit more negative to $E_c$ dissolution rates are much higher than the corresponding values calculated from extrapolation of Tafel lines of anodic curves in both acidified sulphate solution (Fig.5) and neutral solutions of ammonium sulphate (Fig. 6). In the vicinity of $E_c$ dissolution rate is almost independent of potential and grows with a decrease in pH and increase in concentration of ammonium sulphate (Fig.7).
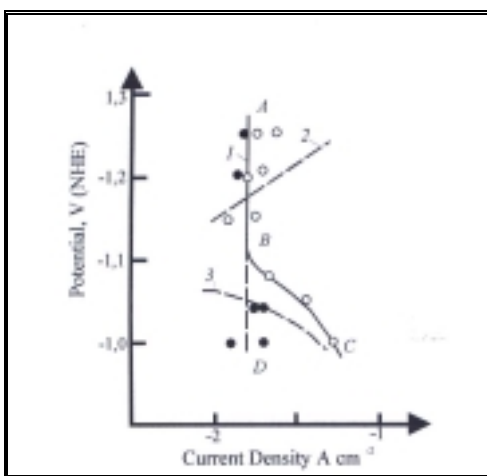


Fig. 5 – Variation of dissolution rate of Mn (o) and of hydrogen evolution rate[*] with potential in 0,1 $NH_2SO_4$ , 2,3 – cathodic and anodic polarization curves corresponding.

Taking into account reaction orders calculated from the data given in Fig.7 the kinetic equations for dissolution reactions in acidified sulphate and neutral ammonium sulphate solutions can be described as follows:

$$i_2^a = K_2 (C_{H+})^2 \quad (2)$$
$$i_2^n = K_2 (C_{NH4+})^2 \quad (3)$$

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[*] calculated as $i_T - i_C$, where $i_T$ - is the total amount of evolved hydrogen gas and $i_C$ – is the amount of hydrogen, calculated from the amount of electricity flowing through the cathode at corresponding potentials.

At more negative potentials the rate of dissolution of manganese decreases with an increase in cathodic overvoltage. However at higher overvoltages dissolution rate is again independent of potential (Fig. 6).
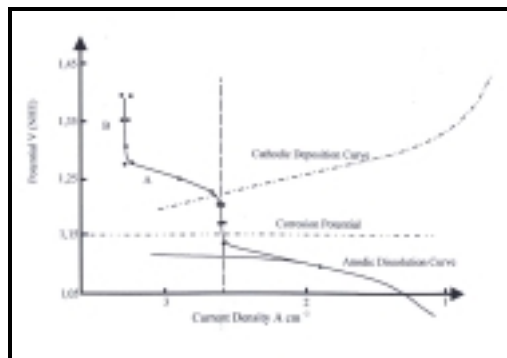


Fig. 6 – Variation of Mn dissolution rate with potential in 6,6 g.l.$^{-1}$($NH_4$)$_2SO_4$ + 232 g.l $^{-1}$ $Na_2SO_4$, pH=6,8 and partial deposition curve in 75,5 g.l $^{-1}$ Mn $SO_4$ + 19,8 g.l $^{-1}$ ($NH_4$)$_2SO_4$

It is important to note that the amount of hydrogen gas evolved during cathodic polarization of manganese in both solutions is higher than the corresponding figures calculated from the amount of electricity under the assumption of 100% current yield of hydrogen gas. What is even more peculiar is that excess of the volume of hydrogen over calculated data is also significant under anodic polarization (Fig. 5 ).
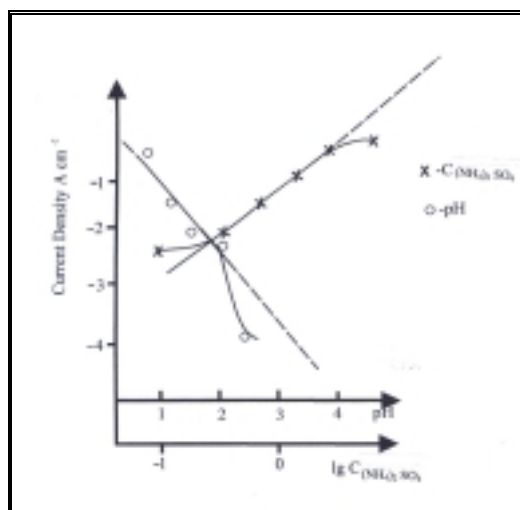


Figure 7 – Dependence of dissolution rate of Mn on concentration of ammonium ions at –1,20 V in XM ($NH_4$)$_2SO_4$ + (2,5 – X) M $K_2SO_4$, 25$^0$ C. (Rate of rotation of Mn disk 2400 rev. min $^{-1}$)

and pH in XN $H_2SO_4$ + (1-X)N $Na_2SO_4$, $25^0$C at-1,25V.

## Structure of manganese deposits

The microstructure of manganese deposits varies with overvoltage (Fig. 8,9). An increase in cathodic potential from -1,50 to -1,52 V (region–A, Fig.3) results in a fivefold increase in crystallite size (Table 1). At potentials corresponding to maximum CY deposits are characterized by large crystals with grain size up to 25 mkm. Opposite trend is observed in region B. However at high overvoltages (region D) crystallites with grain size of 20 mkm are observed.
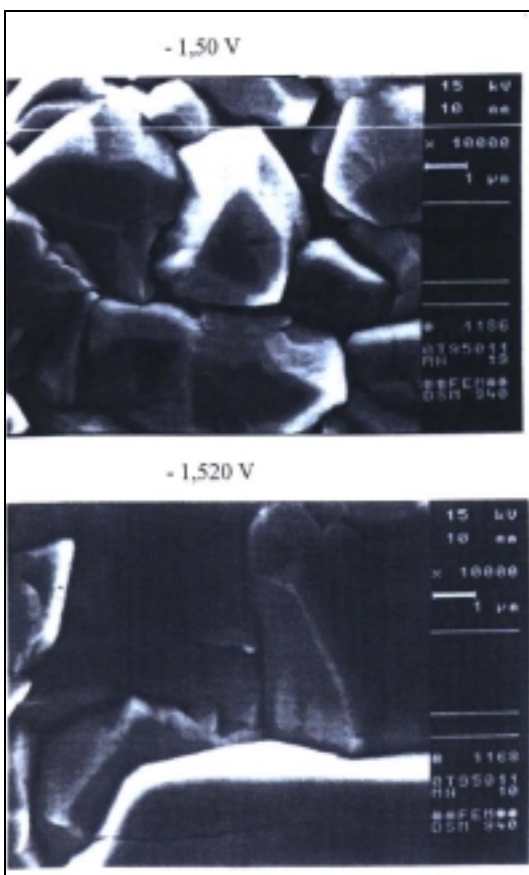


Figure 8 –Effect of potential on microstructure of manganese deposits

Variation in overvoltage affects also allotropic modification of manganese deposits. At low overvoltages cathodic metal is characterized by a simple tetragonal structure and high plasticity due to which manganese is easily stripped from the substrate. It is common approach to identify such deposits as • – modification of manganese. At higher

overvoltages traces of more complex crystal structure characterized by cubic volume-centered lattice consisting of 58 atoms of metal were observed. The fraction of • -Mn in the deposits increases with an increase in overvoltage[11].

## Discussion

### *Effect of Dissolution Reaction*

A specific effect of dissolution of manganese on the process of electrodeposition of manganese was recognized at an early stage of the studies of the kinetics of manganese electrode[6,10]. The absence of the cathodic protection and CY of hydrogen higher than 100% at potentials negative and positive to
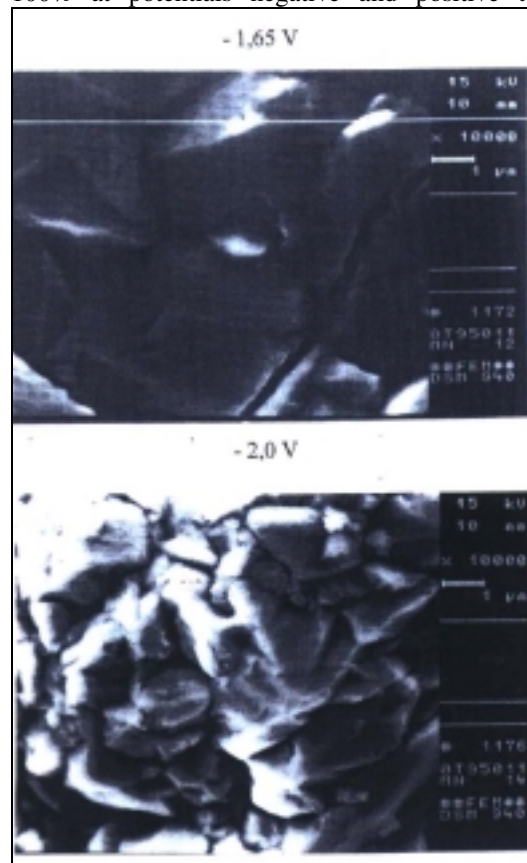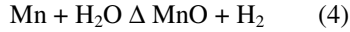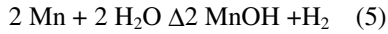


Figure 9 –Effect of potential on microstructure of manganese deposits

corrosion potential were explained by high chemical reactivity of metal and its strong affinity to oxygen due to which manganese chemically reacts with solvent molecules
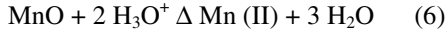
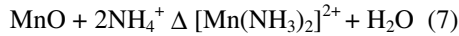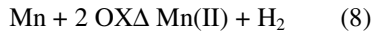liberating hydrogen gas and forming surface oxides / hydroxides:

$$Mn + H_2O \Delta MnO + H_2 \qquad (4)$$

or

$$2\,Mn + 2\,H_2O \Delta 2\,MnOH + H_2 \quad (5)$$

In the presence of oxidizer ($H^+$) or complexing agent ($NH_4^+$) surface film can be slowly (in relation to oxidation reaction) reduced:

$$MnO + 2\,H_3O^+ \Delta Mn\,(II) + 3\,H_2O \qquad (6)$$

or

$$MnO + 2NH_4^+ \Delta [Mn(NH_3)_2]^{2+} + H_2O \quad (7)$$

The overall dissolution reaction can be described as follows:

$$Mn + 2\,OX \Delta Mn(II) + H_2 \qquad (8)$$

which explains experimental reaction orders of dissolution reaction in respect to hydrogen and ammonium ions (eq. 2 and 3), evaluation of extra amount of hydrogen gas (parallel to electrochemical reaction of hydrogen discharge from $H_3O^+$, $H_2O$ or $NH_4^+$ spices) at potentials negative and positive to $E_c$ and independence of the dissolution rate from potential in the vicinity of $E_c$.

In ammonium sulhpate solutions free from manganese salts manganese ions formed in reaction (8) may diffuse to the bulk of the solution at the rate

$$i_3 = K_3[C_{Mn(II)}]_s , \qquad (9)$$

where $[C_{Mn(II)}]_s$ is the concentration of manganese ions at the interface, and to discharge at the cathode according to modified equation 1:

$$i_1 = K_1[C_{Mn(II)}]_s^{1,6} \exp(-2FE/RT) \quad (10)$$

Under steady state conditions:

$$i_2 + i_4 = i_1 + i_3 , \qquad (11)$$

where $i_4 = K_4 \exp(2FE/3RT)$ is the rate of anodic dissolution of manganese in ammonium sulphate solutions [6,7].

Solution of equation (11) under the assumption that $C_{Mn(II)}$ is close to zero in the bulk of the solution leads to the following expression for overall dissolution rate of manganese in neutral ammonium sulphate electrolytes:

$$i. = K_3(C_{NH_4^+})^2 + K_4\exp(2FE/3RT) \,/K_3 + K_1\exp(-2FE/RT) \quad (12)$$

Equation (12) makes it possible to give a correct description of the observed kinetic data. For example, at potentials more negative to $E_c$ term $i_4$ decreases exponentially and becomes negligible at potentials 50 mV negative to $E_c$.

Under these conditions the overall dissolution rate is determined by term $i_3 = K_3(C_{NH_4^+})^2$ which leads to potential independent dissolution of manganese (Fig.6). At high cathodic overvoltages increasing contribution of term $i_1$ (rate of deposition of manganese) leads to linear decrease in dissolution rate with negative slope of Tafel line of 2,3RT/2F. The appearance of the second region where dissolution rate is independent of potential is apparently due to kinetic limitations of manganese deposition reaction at high over-voltages.

Thus the true partial rate of dissolution of manganese is independent of potential in the whole region of potentials. Deviations are due to contribution of deposition rate of dissolved Mn (II) ions to the overall dissolution rate. According to experimental data this effect is less pronounced under stirring conditions due to a decrease in concentration of $[Mn(II)]_s$ as a result of forced diffusion of manganese ions from the interface into the bulk of solution.

### Nature of Kinetic Limitations

It is reasonable to assume that the formation of oxide/hydroxide layer results in an increase in overvoltage of manganese ions discharge reaction

$$[MnX]^{2+} + 2e \Delta Mn + X \quad (13)$$

(where $X \cdot H_2O$, $SO_4^{2-}$ or $NH_3$ depending on solution composition and overvoltage), which otherwise proceeds reversibly[6,7]. Thus overall kinetics of deposition reaction is determined by the balance between rates of manganese oxidation and activation reactions.

Since removal of oxide/ hydroxide layer is assumed to be the slowest and potential independent reaction unfavorable balance between inhibition and activation reactions at sufficiently negative potentials may lead to kinetic limitations of the overall rate of deposition reaction (region of first limiting current, Fig.3), and change in crystal structure of deposits (Fig.8).

Additional effect on inhibition/ activation balance may be due to electrochemical reaction of hydrogen evolution. At low overvoltages hydrogen is formed via discharge of water molecules, while at increased overvoltages discharge of ammonium ions becomes more favorable. Taking into account the fact that hydrogen evolution reaction proceeds at partly oxidized surface it is reasonable to assume that discharge reaction is accompanied by the

reduction of inhibiting layer, e.g. according to overall reaction:

$$MnOH + 2NH_4 + 3e \bullet Mn + H_2 + 2NH_3 + OH^- \quad (14)$$
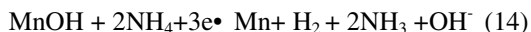
which results in farther acceleration of deposition reaction (region C, Fig.3).

### Catalysis of Hydrogen Evolution Reaction

In sulphate solutions free from Mn(II) ions reaction of discharge of ammonium ions is characterized by apparent transfer coefficient close to 0,5, which is typical for cathodic processes under charge transfer limitations. However, when this reaction proceeds parallel to manganese discharge reaction, catalysis of hydrogen evolution reaction takes place which is expressed in an increase in apparent transfer coefficient to 2, i.e. the kinetic parameters of hydrogen evolution reaction become similar to those, which are characteristic for manganese deposition reaction [12].

This effect can be reasonably explained on the basis of inhibition/activation model described above. Actually the formation of MnOH particles participating in hydrogen evolution reaction (14) is governed by parallel manganese deposition (13) and oxidation (5) reactions. Since reaction (13) is assumed to proceed at the highest rate it should be expected that hydrogen evolution reaction will follow the same kinetic regulations as reaction (13).

### Effect of Selenium Salt

On the basis of this model an enhancement of manganese deposition reaction in the presence of selenium salt can be attributed to stabilization of active form of manganese deposits. It was found that the addition of selenium salt to sulphate solutions results in a decrease in the rate of chemical dissolution of manganese[6,7] possibly as a result of selenium deposition at active manganese atoms, preventing thus further oxidation of manganese.

However the effect of selenium is more complex and results in the change of allotropic modification of manganese from • to • [11]. The same effect is observed with an increase in overvoltage. The detailed analysis of these effects is out of the scope of this paper, however it is obvious that interaction of manganese with hydrogen promoted by selenium and the modification of lattice structure become the dominant factor at high overvoltages.

## Summary

A model for electrodeposition of manganese at low and medium overvoltages was developed. The model is based on the assumption that the kinetics of manganese deposition reaction is determined by a balance of inhibition and activation reactions. The limitation of deposition rate is of kinetic nature and is due to unfavorable ratio of the rates of surface oxidation reaction, resulting in an increase in overvoltage of manganese deposition reaction and of the reaction of removal of oxidized layer leading to the activation of deposition reaction. Parallel hydrogen evolution reaction proceeds via both chemical and electrochemical reactions. The latter also leads to the weakening of kinetic limitations due to simultaneous reduction of inhibiting layer. Ammonium ions play important role not only as a buffer, but mostly as an activator of the surface of the cathode.

## References

1. *R.S.Dean*, Electrolytic Manganese and its alloys, Ronald Press Co, N.Y.1952
2. *R. Agladze*, Metallurgy, **9**, 15 (1939)
3. *I. Shaoshvili, R. Agladze, K.Demetrashvili, Bull. Acad. Sci Georgia, **121**, 345 (1986)*
4. *M. Sugiama et al, Plating & Surface Finishing **74, 77 (1987)***
5. *T. Agladze, EAST-Report, Jeh. Cmund, 1993, p.109.*
6. *T.Agladze*, Electrochemical Behaviour of Manganese In Aqueous Electrolytes, Dissertation, Karpov Institute of Physical Chemistry, Moscow; 1969.
7. *T.Agladze, Y.M.Kolotyrkin*, Proc. USSR Electrochemical Meeting, **2**, Moscow; 1969, p.3.
8. *K.E.Heusler, M.Bergmann*, Electrochemica Acta, **15**, 1887, (1970)
9. *Ya. M. Kolotyrkin, T.Agladze*, Zaschita Metallov (Metal Protection), **3**, 413 (1967)
10. *T. Agladze, Ya.M. Kolotyrkin*, Zaschita Metallov (Metal Protection), **4**, 721 (1968)
11. *N. Dhanajayan, T. Banerjee*, Structure of Electro-Deposited Manganese, CSJR, Jamshedrup, India, 1969, p.47.
12. *Ju. M. Loshkarjev*, Ukr.Khim Zhurnal, **14**, 918**,** 1963