



STUDYING THE EFFECT OF COMPOUNDS IN THE MANGANESE COMPOSITES ON MANGANESE ELECTROLYSIS BY VOLTMETER-AMMETER METHOD

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ABSTRACT

In this paper, the reduction of Mn(II) ions on titanium electrode in neutral medium was studied through voltmeter-ammeter method. In the medium mentioned above, reduction potential of Mn(II) ions was determined by cathode-anode cyclic polarization curve. The result of voltmeter-ammeter method enables us to investigate the effect of manganese compositions in the industrial solutions on magnesium electrolysis. The effect of the compounds in the industrial solution (Co, Ni, Cu, Fe) on the decrease of ultrahigh voltage with hydrogen release was found by potentiodynamic polarization curves.

On the potentiodynamic polarization curves of various concentrations of zinc ions (10, 20, 30, 40 mg/dm³), – 1280 mV – 1300 mV potential discharging current can be seen in cathode area. To measure this potential discharging current cathode-anode cyclic polarization curve was illustrated. On the anode region, reoxidizing current of the reduced zinc was measured to be +980 and +1200 mV on the surface of the electrode. It was found that more zinc (II) ions than 10 mg/dm³ might contaminate the cathodic manganese. Among the compounds, which were investigated in our study, little amount of cobalt ions decrease sharply the yield of electric of Mn(II) discharging ions on cathode. Only 8 mg/dm³ of cobalt ions in the electrolyte shift the separation potential of hydrogen from – 1600 mg/dm³ to – 1580 mg/dm³. Such declining the overpotential of hydrogen release sets a limit to reduction of manganese cathode.

Key words: Electrolyte, Polarization curves, Manganese, Cathodic reduction, Potential recovery.

INTRODUCTION

Manganese occupies the fourth place in application after iron, aluminum, and copper. Manganese is very important metal for iron and steel production due to its deoxidizing and

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alloying properties. And also, manganese is a key component for making low-cost stainless steel. Small amount of manganese added to steel to enhance the steel workability at high temperature and tensile strength. Higher amount of manganese (about 8 %) is added to steel to increase the steel wear resistance. One particular type of steel can be produced by adding 12% of manganese to steel, usually known as Hadfield manganese steel. This steel often used for gears, minerals and mining equipment, grinding and crushing and many others. As well as, approximately 15% manganese added to ferromanganese alloy¹. The manganese added to steel for the purpose of increasing the steel properties should be pure enough so that we can achieve our goal. The best way of making pure manganese is electrolysis².

Hydrometallurgical method for manufacturing manganese from its ore or technologically wastes has been widely applied lately. That is why to study the technology of physico-chemical concepts of obtaining the electrolytic manganese is getting more and more important.

EXPERIMENTAL

Methods of investigation

Electrochemical properties of manganese (II) ions aqueous solution were studied with “P8” potentiostat by potentiodynamic polarization curves. Voltmeter-ammeteric studies carried out in three-electrode, separated cathode-anode region thermostat electrolysis. Silver-chlorine electrode, soaked in saturated solution of KCl ($E = +203$ mV), was used as a reference electrode and widened platinum wire electrode. For working cathode electrode, titanium wire with coated Teflon with a diameter of 4 mm was used.

RESULTS AND DISCUSSION

Potential of manganese relatively electronegative, so many parameters can cause to deoxidize the metal ions on cathode. They might be: composition of electrolyte, cathodic and anodic materials, temperature, pH of electrolytes and etc. and they may lead to contaminate cathodic manganese, reducing manganese makes decrease the electric (current) yield or they can make manganese never reduced on cathode³. For this purpose, these parameters should be investigated.

In this paper, we studied the reducing potentials of aqueous solution of manganese (II) ions on titanium electrode by potentiodynamic polarization curves. According to polarization curves according to taken waves from -1400 mV potential value manganese ions could be reduced, and further from -1600 mV hydrogen ions begin to reduce (Fig. 1).

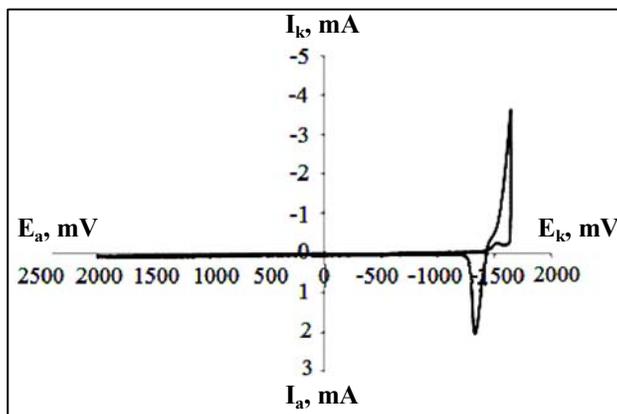


Fig. 1: Cathodic-anodic potentiodynamic polarization curve
 $[\text{Mn}^{2+}] = 36 \text{ g/dm}^3$, $[(\text{NH}_4)_2\text{SO}_4] = 160 \text{ g/dm}^3$, $V = 100 \text{ mV/s}$, $T = 25^\circ\text{C}$

When we shift the potential from cathode to anode, the manganese deposited from -1400 mV will re-oxidize again. As can be seen from the curves the higher overpotential of hydrogen release from titanium electrode, indicating that titanium electrode will be efficient to use as cathodic material.

Concentration of ammonium sulfate acting as a bufferic agent, main component of manganese electrolyte, indicated variously in literature^{4,5}.

In Z. Iankelevich's works the optimum concentration of ammonium sulfate and manganese was $125\text{-}150 \text{ g/dm}^3$. In R. Aglazde's studies ammonium sulfate it was $100\text{-}150 \text{ g/dm}^3$, while in Allmand and A. Kempbell's work it should be 100 g/dm^3 . To determine the exact value, ammonium sulfate was investigated in different concentration ($20\text{-}160 \text{ g/dm}^3$) with manganese sulfate solution on titanium electrode, by cathodic polarization curves (Fig. 2). As shown in the figure increasing of ammonium sulfate can be seen by increasing the maximum of reduced manganese (II) ions. Thus, increasing of the ammonium sulfate in solution increased the electro conduct of the electrolyte, which decreases the electro voltage and decreases the electro waist. But, addition of ammonium sulfate more than indicated volume could be form complex salt with manganese.

Oxidizing potential of manganese relatively electronegative (-1.180), so it is very sensitive to the amount of compounds in the solution.^{6,7} Electrolysis of industrial solutions may have many compounds. It could be found that a trace amount of cobalt ions affect the reducing of manganese (II) ions. As can be seen from the picture only 8 mV/dm^3 amounts of cobalt can lower the releasing potential of hydrogen from -1600 – to 1580 mV , $40\text{-}72 \text{ g/dm}^3$

amounts of hydrogen shifted to -1250 , -1350 mV. This hydrogen releasing current deters manganese reduce on cathode. This phenomenon also occurs in the solution of zinc ions (Fig. 4). If the concentration of nickel ions around 40 - 45 g/dm³, it reduces hydrogen from -1600 mV to 1450 mV compared to the reference solution.

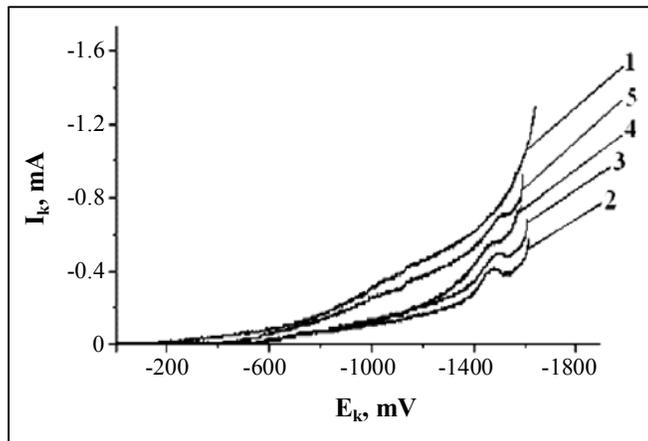


Fig. 2: Cathodic potentiodynamic polarization curve of various concentration of ammonium sulfate in manganese (II) sulfate solution on titanium electrode

$[\text{Mn}^{2+}]$ 12 g/dm³, $V = 100$ mV/s, $T = 25^\circ\text{C}$.

1 – reference $[(\text{NH}_4)_2\text{SO}_4]$ 160 g/dm³; $[(\text{NH}_4)_2\text{SO}_4]$ g/dm³: 2 – 20; 3 – 40; 4 – 80; 5 – 160;

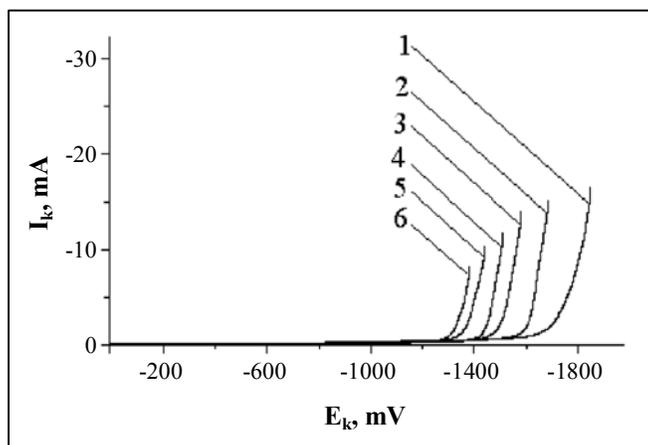


Fig. 3: Cathodic polarization curves of various concentrations of cobalt ions on titanium electrode

$[(\text{NH}_4)_2\text{SO}_4]$ 160 g/dm³, $V = 100$ mV/s $T = 25^\circ\text{C}$

$[\text{Co}^{2+}]$ mg/dm³: 1 – reference; 2 – 8; 3 – 24; 4 – 40; 5 – 56; 6 – 72.

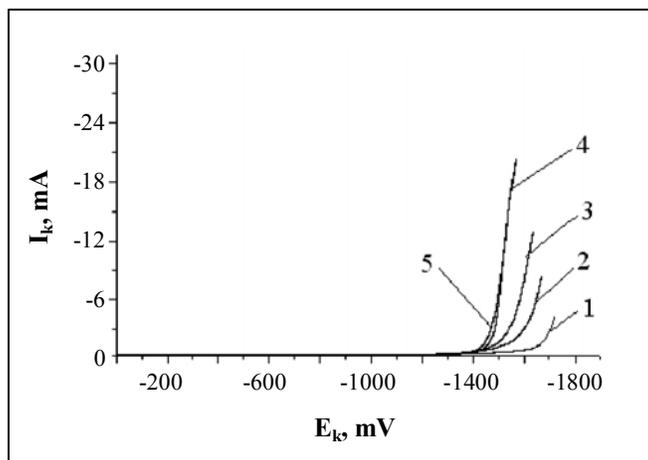


Fig. 4: Cathodic polarization curves of various concentrations of nickel ions on titanium electrode

$[(\text{NH}_4)_2\text{SO}_4]$ 160 g/dm^3 , $V = 100 \text{ mV/s}$, $T = 25^\circ\text{C}$.
 $[\text{Ni}^{2+}] \text{ mg/dm}^3$: 1 – reference; 2 – 10; 3 – 20; 4 – 40; 5 – 45.

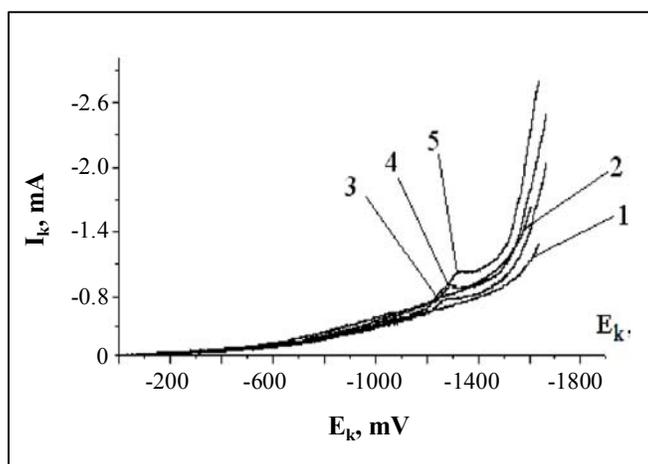


Fig. 5: Cathodic polarization curves of various concentrations of zinc ions on titanium electrode

$[(\text{NH}_4)_2\text{SO}_4]$ 160 g/dm^3 , $V = 100 \text{ mV/s}$, $T = 25^\circ\text{C}$.
 $[\text{Zn}^{2+}] \text{ mg/dm}^3$: 1 – reference; 2 – 10; 3 – 20; 4 – 40; 5 – 60.

By the cathode-anode cyclic curves (Fig. 6), it can be seen that maximum of reducing current in cathode is being re-oxidized on anode (980-1200 mV). It can be estimated that red-ox maximums could be same with red-ox potential of zinc (II) ions in the electrolyte.

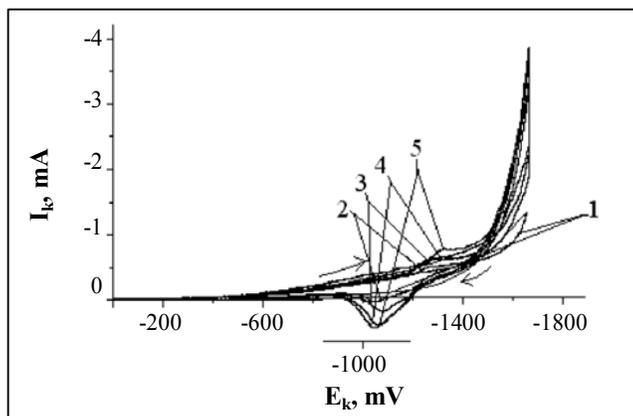


Fig. 6: Cathode-anodic polarization curves of various concentrations of zinc ions on titanium electrode

$[(NH_4)_2SO_4]$ 160 g/dm³, $V = 100$ mV/s, $T = 25^0C$.
 $[Zn^{2+}]$ mg/dm³: 1 – reference; 2 – 10; 3 – 20; 4 – 40; 5 – 60.

We also investigated positively charged copper and iron ions, which could be present in the manganese based industrial solution and could influence the electrolysis of manganese by the method of potentiodynamic polarization curves (Fig. 7 and 8). As can be seen on the picture only 5 mg/dm³ concentration of copper ions decrease sharply the cathodic reduces of manganese by current yield and shift the hydrogen release to right side. The effect of iron (II) ions to manganese oxidizing could be found in the range of 20-40 mg/dm³.

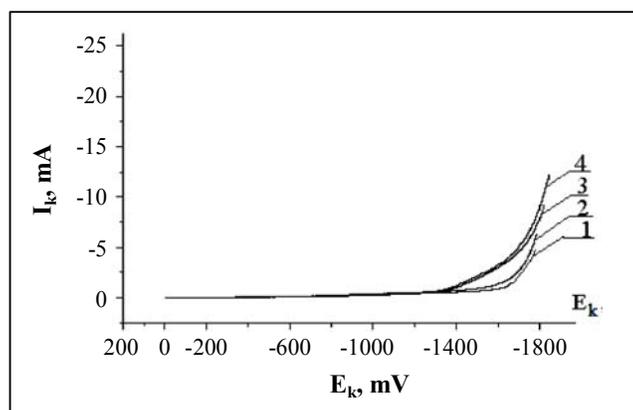


Fig. 7: Cathodic polarization curves of various concentrations of copper ions on titanium electrode

$[(NH_4)_2SO_4]$ 160 g/dm³, $V = 100$ mV/s, $T = 25^0C$
 $[Cu^{2+}]$ mg/dm³: 1 – reference; 2 – 2.5; 3 – 5; 4 – 7.5

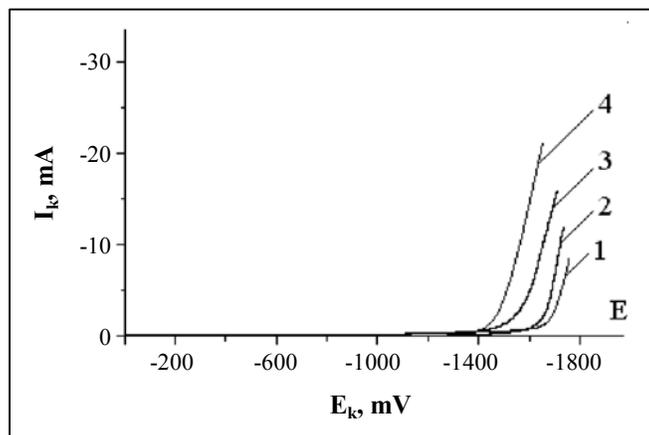


Fig. 8: Cathodic polarization curves of various concentrations of iron ions on titanium electrode

$[(\text{NH}_4)_2\text{SO}_4]$ 160 g/dm³, $V = 100$ mV/s, $T = 25^\circ\text{C}$
 $[\text{Fe}^{2+}]$ mg/dm³: 1 – reference; 2 – 20; 3 – 40; 4 – 60.

CONCLUSION

In this paper, we investigated the influence of various ions in the industrial solution and their effect for manganese (II) ions electrolysis on titanium electrode. Through the findings of our work, it was proved that the lower concentration of indicated ions in the solution could help to increase the yield of current and obtain pure manganese.

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