

Electrochemically Synthesis of the Pirazine-2,3-Dicarboxylic Acid. Cyclic Voltammetry Studies on Cooper Electrode

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Abstract: The previous studies shows that the KMnO_4 regeneration used in chemical oxidation of chinoxaline to form the pyrazine-2,3-dicarboxylic acid is possible on platinum in chinoxaline absence[1] or his presence[2] and on nickel electrode[3]. The purpose of this paper is investigation of the KMnO_4 regeneration process on copper electrode. The studies was made by cyclic voltammetry at a concentrations of support electrolyte (KOH) of about 5 to 10%, at 25-40°C temperature, KMnO_4 concentration until $6 \cdot 10^{-2}$ M and maximum concentration of quinoxaline until $2.61 \cdot 10^{-2}$ M in electrolite solution. On copper electrode it's possible the process of oxidation of Mn^{6+} to Mn^{7+} . Anodic regeneration of Mn^{7+} is favoured by rise of : KOH concentration, temperature, Mn^{7+} and Mn^{6+} concentration, quinoxaline.

Keywords: electrochemistry, cyclic voltammetry, quinoxaline, pirazine-2,3-dicarboxylic acid, cooper electrode.

1. Introduction

Previous studies demonstrated that regeneration of the KMnO_4 used in chemical oxidation of the quinoxaline with formation of the pirazine-2,3-dicarboxylic acid is possible on platinum electrode in the absence [1] and in the presence of quinoxaline [2] and also on nickel electrode [3].

With intention to enlarge the area of the usable anodes in this process and to identify the best material for the anode, in this paper we investigated through cyclic voltammetry the cooper behaviour.

2. Experimental

In order to realize the studies we used the same electrolysis cell used previously [1, 2, 3], equipped with three electrodes – a platinum counter electrode, a reference SCE electrode and the working electrode was maded from cooper. We used a cooper wire having the section of 0.031 cm^2 . The electrode was cleaned before every determination through diving in diluted nitric acid and then into an oxalic acid solution into sulphuric acid 20% - approximately 10 minutes time. The electrode treated in this way was utilised in a series of determinations. Sometimes – when the results were not accurate – was necessary to repeat the cleaning process.

The other work conditions were the same with those used in the study of platinum electrode [1, 2].

The cyclic voltammetry studies where made using a potentiostat model PGZ 301 DynamicEIS Voltammetry-Radiometer Copenhagen, equipped with software VoltaMaster 4. As base electrolyte we used KOH, solution with 5% and 10% concentrations, at 25 and 40° C temperatures. The concentration of the potassium permanganate and quinoxaline solutions (solutions into KOH with the same concentration with the one used in

actual determinations – 5 and respectively 10 %) was 1N and respectively 0.5 M. Work interval: 0 - +800mV.

Polarisation speed was 100 mV/s. Every time was kept the third traced voltammogram. All the potentials in this paper are reported at SCE, if nothing else is specified.

3. Results and discussion

The results obtained working on cooper electrode, at 25° C, in KOH 5% solution, at various concentrations of KMnO_4 , are presented in figure 1.

At curve 1 traced in the absence of the Mn^{7+} ions is evidenced only oxygen formation starting from 670 mV potential and on return, a cathodic peak – well defined – at 540 mV.

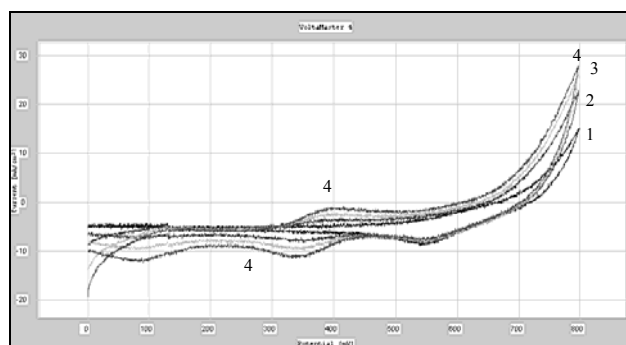


Figure 1. Cooper electrode, T = 25°C, KOH 5% sol, KMnO_4 concentration: 1 – 0, 2 - $2 \cdot 10^{-2}$ M, 3 - $3.8 \cdot 10^{-2}$ M, 4 - $6 \cdot 10^{-2}$ M.

The introduction of the Mn^{7+} ions into the electrolyte solution leads to the formation of an anodic peak at proximate 400 mV and two cathodic peaks at 340 mV and respectively 80 mV. The peaks – anodic and cathodic – at 300 – 400 mV correspond to a reversible process:



The other anodic peak – at 80 mV – is associated with Mn^{4+} reduction.

The intensity of all the peaks increase with Mn^{7+} concentration and in the same time the peak potentials shift to more negative values.

The increase of the Mn^{7+} concentration do not affects the cathodic peak that initially appeared on the base curve – peak that could be due to the reduction of the cooper compound, probably an oxide.

The effect on the oxygen formation, of the increase of the Mn^{7+} concentration is make the curves to shift to more negative potentials, shift that is proportional with the concentration.

Is obvious that Mn^{6+} to Mn^{7+} oxidation, accordingly KMnO_4 regeneration, is possible on the cooper electrode too.

The increase of the Q concentration in the electrolyte solution (figure 2) do not modifies the peaks highlighted in the figure 1 but lead to the depolarization of oxygen formation, depolarization which is proportional with concentration of Q. This differ to the situation observed on platinum and nickel electrode where the effect of Q into the electrolyte was similar with the addition of the Mn^{7+} .

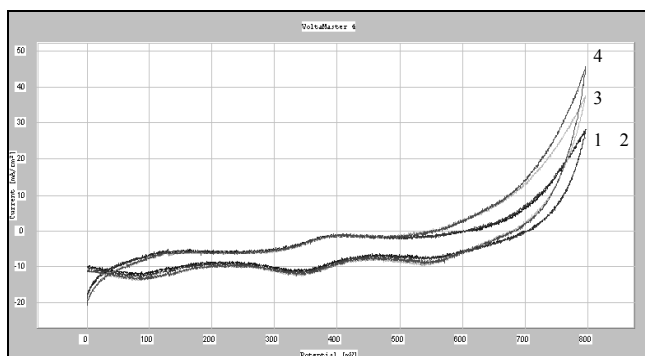


Figure 2. Cooper electrode, $T = 25^\circ\text{C}$, sol. KOH 5%, KMnO_4 concentration is $6 \cdot 10^{-2}\text{M}$, Q concentration: 1 – 0, 2 – $1.18 \cdot 10^{-2}\text{M}$, 3 – $2.04 \cdot 10^{-2}\text{M}$, 4 – $2.61 \cdot 10^{-2}\text{M}$.

The temperature increase to 40°C , in KOH 5% solution at increasing of the KMnO_4 concentrations lead to the results presented in figure 3.

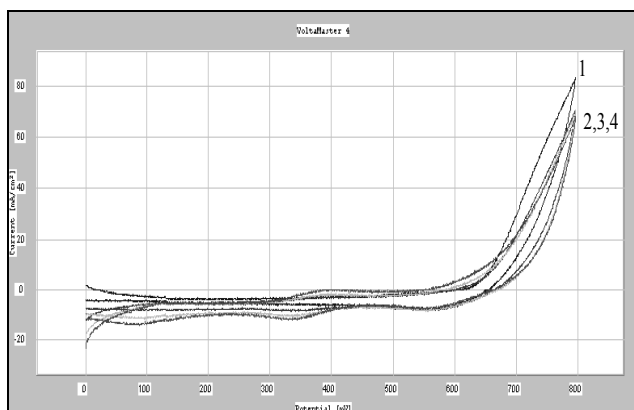


Figure 3. Cooper electrode, $T = 40^\circ\text{C}$, sol. KOH 5%, KMnO_4 concentration: 1 – 0, 2 – $2 \cdot 10^{-2}\text{M}$, 3 – $3.8 \cdot 10^{-2}\text{M}$, 4 – $6 \cdot 10^{-2}\text{M}$.

Regarding oxygen formation, the presence of the Mn^{7+} ions has the effect to polarize the process. But analyzing the peaks that it's formed in the Mn^{7+} presence, we observe the appearance of the peaks characteristic to the reversible process $\text{Mn}^{7+}/\text{Mn}^{6+}$ and the reduction peak of the Mn^{4+} . The peaks bring up with the increase of the Mn^{7+} concentration.

The Q presence (figure 4) produce a slightly increase of the anodic peak, therefore it seems that Mn^{6+} to Mn^{7+} oxidation is favoured. The oxygen formation it's again shifted to more positive potentials – suffer a polarization process – it is disfavoured, hereby in the presence of the manganese ions the interval usable for utile processes (for example Mn^{6+} oxidation) it is more extended at 40°C .

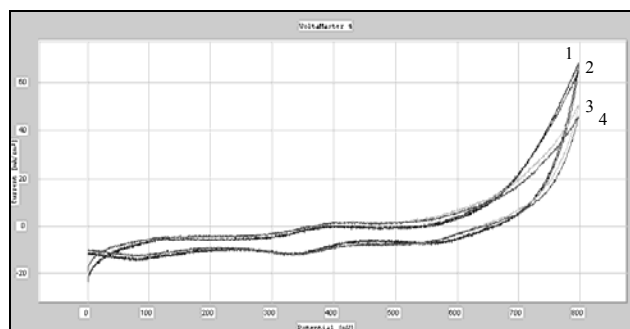


Figure 4. Cooper electrode, $T = 40^\circ\text{C}$, sol. KOH 5%, KMnO_4 concentration is $6 \cdot 10^{-2}\text{M}$, Q concentration: 1 – 0, 2 – $1.18 \cdot 10^{-2}\text{M}$, 3 – $2.04 \cdot 10^{-2}\text{M}$, 4 – $3.62 \cdot 10^{-2}\text{M}$.

The increase of the KOH concentration at 10% into the electrolyte solution, led to the curves presented in figure 5. The increase of the Mn^{7+} concentration leads to the formation of the same peaks whichever we mentioned when the KOH concentration was 5% - characteristic to the reversible process $\text{Mn}^{6+}/\text{Mn}^{7+}$ and the cathodic one, of Mn^{4+} reduction. The peaks increase with the concentration and shift slightly to more negative potentials. Such as, the oxygen formation shifts to more negative values.

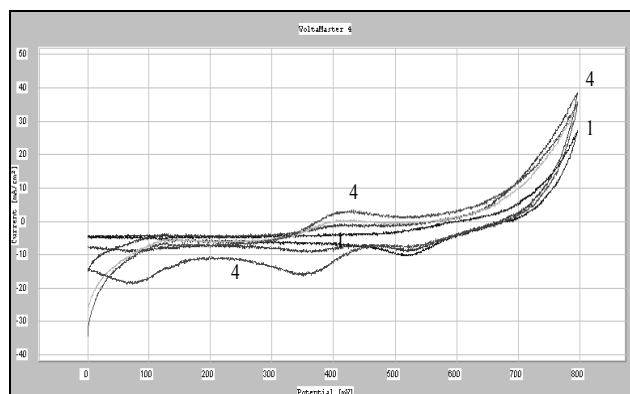


Figure 5. Cooper electrode, $T = 25^\circ\text{C}$, sol. KOH 10%, KMnO_4 concentration: 1 – 0, 2 – $2 \cdot 10^{-2}\text{M}$, 3 – $3.8 \cdot 10^{-2}\text{M}$, 4 – $6 \cdot 10^{-2}\text{M}$.

The presence of Q into electrolyte solution (figure 6), at this concentration of KOH, produce a slight increase of the Mn^{6+} oxidation peak and the decrease of both reduction

peaks – of Mn^{7+} and Mn^{4+} . Hence, it is favoured the Mn^{6+} oxidation, this effect appearing so at the others studied electrodes, platinum and nickel. It seems that the cooper electrode has the same behaviour in the Mn^{7+} regeneration process.

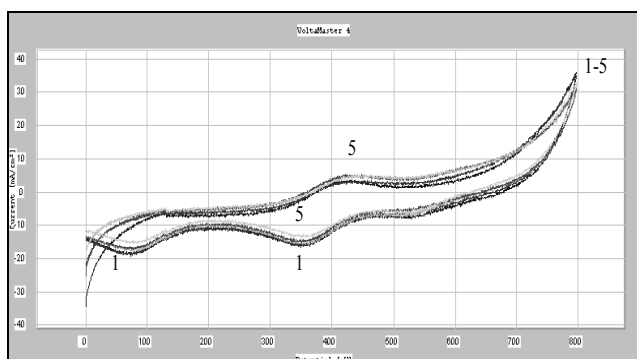


Figure 6. Cooper electrode, $T = 25^\circ C$, sol. KOH 10%, $KMnO_4$ concentration is $6 \cdot 10^{-2} M$, Q concentration: 1 – 0, 2 – $1.18 \cdot 10^{-2} M$, 3 – $2.04 \cdot 10^{-2} M$, 4 – $2.61 \cdot 10^{-2} M$, 5 – $3.62 \cdot 10^{-2} M$.

The increase of the temperature at $40^\circ C$, leads to the results presented in figure 7. The same known peaks it's preserved also at this temperature, peaks that increase with Mn^{7+} concentration. If we compare them with those at $25^\circ C$ we not observe significant differences.

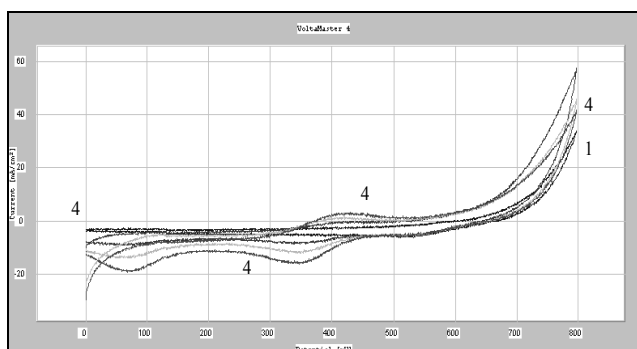


Figure 7. Cooper electrode, $T = 40^\circ C$, sol. KOH 10%, $KMnO_4$ concentration: 1 – 0, 2 – $2 \cdot 10^{-2} M$, 3 – $3.8 \cdot 10^{-2} M$, 4 – $6 \cdot 10^{-2} M$.

The presence of Q leads at curves presented in figure 8.

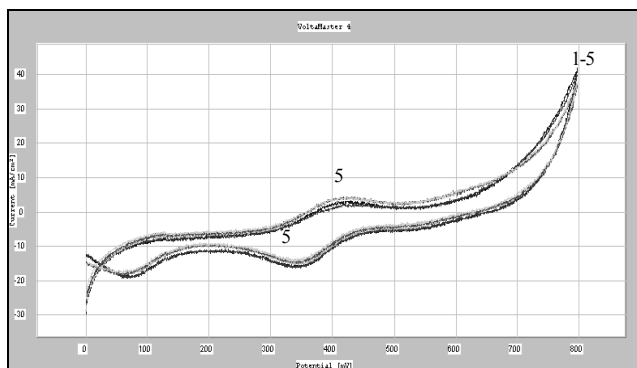


Figure 8. Cooper electrode, $T = 40^\circ C$, sol. KOH 10%, $KMnO_4$ concentration is $6 \cdot 10^{-2} M$, Q concentration: 1 – 0, 2 – $1.18 \cdot 10^{-2} M$, 3 – $2.04 \cdot 10^{-2} M$, 4 – $2.61 \cdot 10^{-2} M$.

Again it's evidenced the increase of the anodic peak and the decrease of the cathodic ones, having the same effect, the relief of the Mn^{7+} regeneration.

The effect due to increase of the KOH into electrolyte solution from 5 to 10 % at $25^\circ C$ it's shown in figure 9.

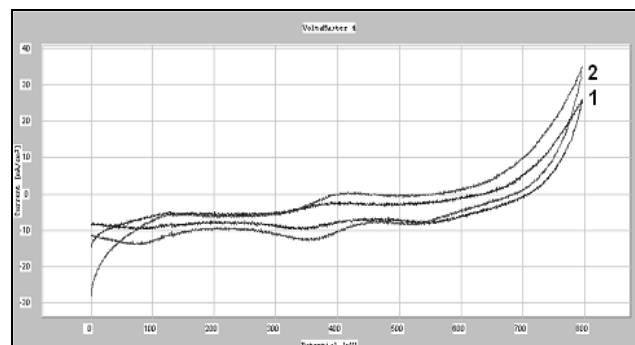


Figure 9. Cooper electrode, $T = 25^\circ C$, $KMnO_4$ concentration is $3.8 \cdot 10^{-2} M$, sol. KOH: 1 – 5%, 2 – 10%.

We observe that with the increase of the KOH concentration into the base electrolyte the oxygen formation shift to more negative potentials and, which is the more important, the intensity of the observed peaks increase. The same effect is observed at $40^\circ C$ (figure 10).

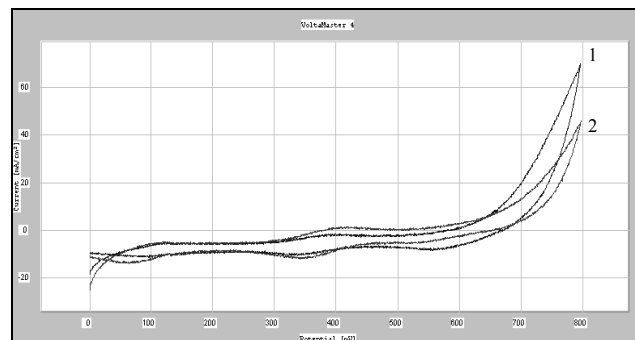


Figure 10. Cooper electrode, $T = 40^\circ C$, $KMnO_4$ concentration is $3.8 \cdot 10^{-2} M$, sol. KOH: 1 – 5%, 2 – 10%.

As well in the presence of Q the increase of the KOH concentration into the electrolyte has the same significant effect – the increase of the peak currents, figures 11 and 12 – at 25 respectively $40^\circ C$.

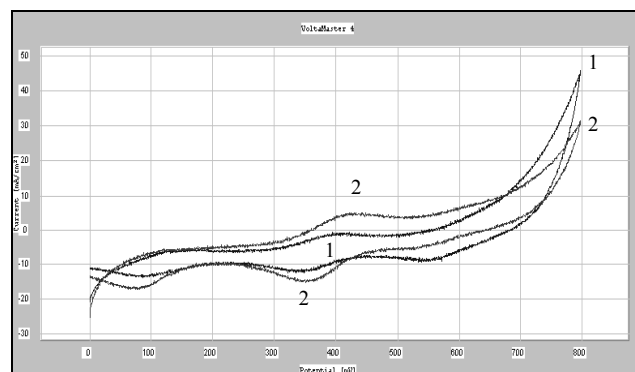


Figure 11. Cooper electrode, $T = 25^\circ C$, $KMnO_4$ concentration is $3.8 \cdot 10^{-2} M$, Q concentration is $2.61 \cdot 10^{-2} M$, sol. KOH: 1 – 5%, 2 – 10%.

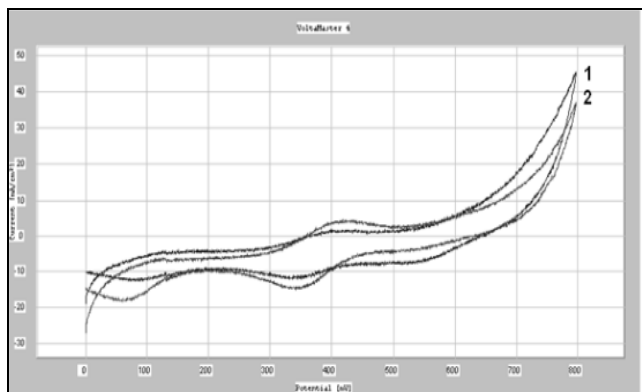


Figure 12. Cooper electrode, $T = 40\text{ }^{\circ}\text{C}$, KMnO_4 concentration is $3.8 \cdot 10^{-2}$ M, Q concentration is $2.61 \cdot 10^{-2}$ M, sol. KOH: 1 – 5%, 2 – 10%.

The effect of the temperature increase to the observed peaks is practically insignificant into KOH 5% and fairly reduced into KOH 10%. In both studied situations, the oxygen formation is much shifted through the more negative potentials – figure 13 and 14.

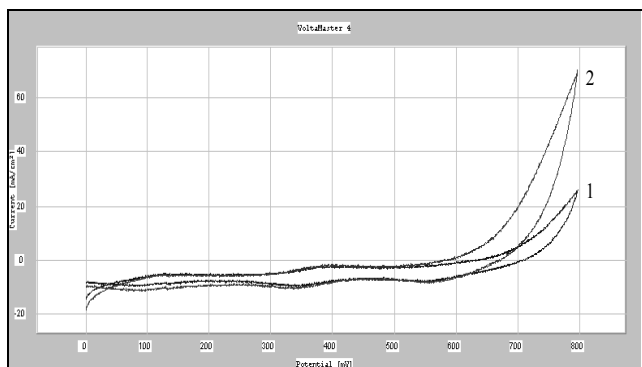


Figure 13. Cooper electrode, KMnO_4 concentration is $3.8 \cdot 10^{-2}$ M, sol. KOH 5%, T : 1 – $25\text{ }^{\circ}\text{C}$, 2 – $40\text{ }^{\circ}\text{C}$.

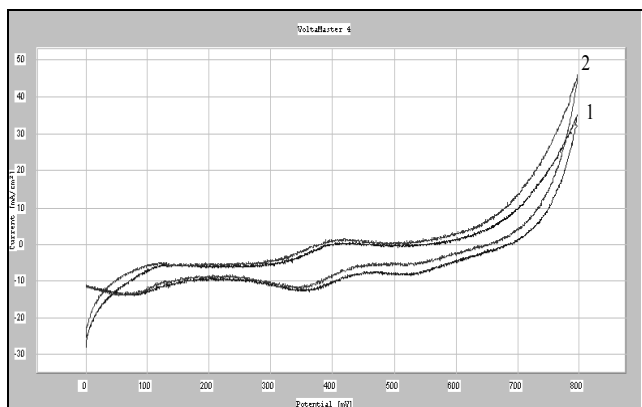


Figure 14. Cooper electrode, KMnO_4 concentration is $3.8 \cdot 10^{-2}$ M, sol. KOH 10%, T : 1 – $25\text{ }^{\circ}\text{C}$, 2 – $40\text{ }^{\circ}\text{C}$.

In the presence of Q, into KOH 5% the temperature effect is presented in the figure 15. In these conditions the effect is fairly accentuated leading at the increase of the anodic peak and to the decrease of the cathodic ones.

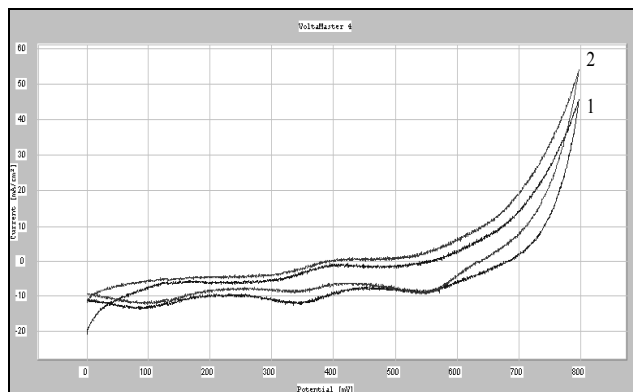


Figure 15. Cooper electrode, KMnO_4 concentration is $3.8 \cdot 10^{-2}$ M, sol. KOH 5%, Q concentration is $2.61 \cdot 10^{-2}$ M, T : 1 – $25\text{ }^{\circ}\text{C}$, 2 – $40\text{ }^{\circ}\text{C}$.

The temperature effect it's less important in KOH 10% solution - figure 16.

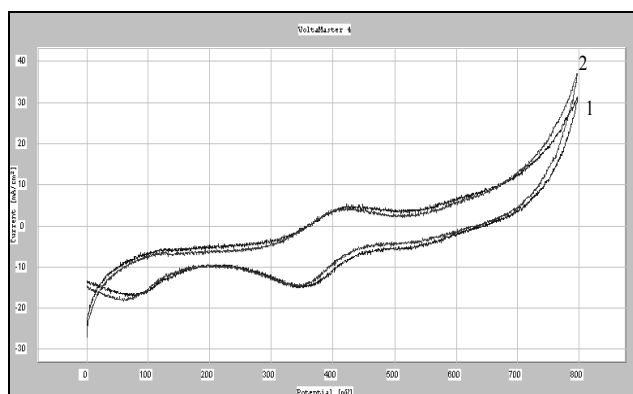


Figure 16. Cooper electrode, KMnO_4 concentration is $3.8 \cdot 10^{-2}$ M, sol. KOH 10%, Q concentration is $2.61 \cdot 10^{-2}$ M, T : 1 – $25\text{ }^{\circ}\text{C}$, 2 – $40\text{ }^{\circ}\text{C}$.

4. Conclusions

In conclusion, we can affirm that the regeneration process of the Mn^{7+} can be realised on copper electrode, besides on platinum and nickel, and is favoured by the increase of the KOH concentration into the electrolyte, by the temperature increase (in special at small concentrations of KOH – at the reaction end), by the increase of the Mn^{6+} concentration and by the presence of Q – but significantly less than in the case of platinum and nickel.

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