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OBTAINING PYRAZINE-2,3-DICARBOXYLIC ACID THROUGH ELECTROCHEMICAL OXIDATION OF QUINOXALINE ON COPPER ELECTRODE

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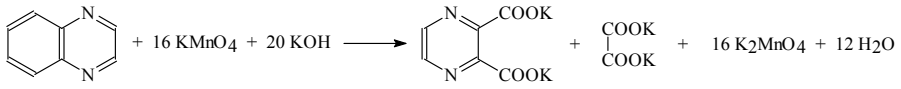
ABSTRACT. In order to improve current knowledge and to expand the variety of electrodes used for the pyrazine-2,3-dicarboxylic acid (PDCA) production process, we investigated the behaviour of the copper anode. A laboratory electrolyser for PDCA synthesis with copper anode using electrochemically regenerated $KMNO_4$ as chemical reagent was manufactured based on results from cyclic voltammetry studies performed on copper electrode. The best performances of this electrolyser are current efficiencies of ~55% and substance efficiencies up to 72% - achieved at a current density of 3,5 A/dm^2. Maximum conversion was 90%.

Keywords: quinoxaline, pyrazine-2,3-dicarboxylic acid, electrolyser, copper electrode, potassium permanganate

INTRODUCTION

The synthesis of pyrazinamide – efficient in tuberculosis treatment – in an advantageous way is of maximum interest [1-3]. The raw material for pyrazinamide manufacture is dipotassium-pyrazine-2,3-dicarboxylic acid (K_2PDCA) which must be obtained by chemical oxidation of quinoxaline (Q) [4-6] with KMnO4 in alkaline medium [7-9].



K_2MnO_4 formed in this reaction is decomposed immediately, form MnO_2 precipitate, which is released and leads to a $KMnO_4$ consumption about 16 kg for each kg of K_2PDCA [10].

Previous studies have shown that the pyrazine-2,3-dicarboxilic acid (PDCA) production process is possible, through quinoxaline chemical oxidation on platinum [11] and nickel [12] electrodes with electrochemically regenerated potassium permanganate ($KMnO_4$). Unlike the platinum electrode – known for

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its stability in strong oxidation and reduction conditions – the copper electrode undergoes a series of chemical transformations when immersed in electrolyte solutions. Thus, in alkaline medium, a layer of $Cu(OH)_2$ is formed on its surface influencing electrode processes. This is why we studied through cyclic voltammetry the behaviour of the copper electrode in electrolyte alkaline solutions with potassium manganate and quinoxaline. Based on study results, a laboratory electrolyser was made for PDCA synthesis on perforated copper plate anode, using electrochemically regenerated potassium permanganate as chemical reagent.

RESULTS AND DISCUSSION

The curves obtained through cyclic voltammetry at 20°C and $0.4 \cdot 10^{-3}$M Mn(VI) concentrations, on copper anode, for different support-electrolyte concentrations, are shown in figure 1.

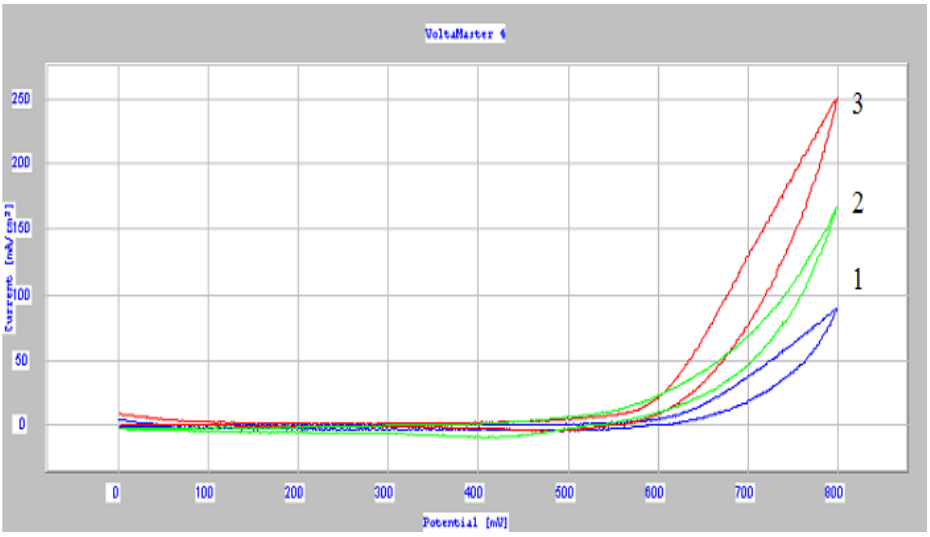

Figure 1. Cyclic voltammograms recorded on the copper electrode, *v* = 100 V/s, T = 20ºC; $0.4 \cdot 10^{-3}$M Mn(VI); KOH solution: 1) – 2M; 2) - 4M; 3) – 8M.

Increase of KOH concentration in the electrolyte solution in the presence of Mn(VI), leads to a significant depolarisation of electrode reactions.

Current density variation at a constant electrochemical potential with temperature and KOH concentration is shown, with and without potassium manganate addition, on the copper electrode, in tables 1 and 2.

Table 1. Current density variation at constant electrochemical potential (700 mV) with electrolyte concentration and work temperature, on the copper electrode, in the absence of Mn(VI).

$i_{[E=700mV]}$ [mA/cm^2]	Temperature (°C)	KOH 2N	KOH 4N	KOH 8N
	20	17,514	60,635	52,639
	45	18,686	81,341	87,936
	55	59,352	126,36	139,76

Table 2. Current density variation at constant electrochemical potential (700 mV) with electrolyte concentration and work temperature, constant concentration of Mn(VI) ($0.4 \cdot 10^{-3}$ M), on the copper electrode.

$i_{[E=700mV]}$ [mA/cm^2]	Temperature (°C)	KOH 2N	KOH 4N	KOH 8N
	20	18,597	65,455	68,777
	45	31,44	92,26	119,3
	55	54,989	126,89	183,3

An increase in temperature and KOH concentration leads to an increase in current density at a constant electrochemical potential and to oxygen release depolarisation. By comparing this depolarisation with the one observed in the absence of potassium manganate one can see a 30% increase in current at constant electrochemical potential (700 mV). This increase shows that there is another process taking place on the electrode at electrochemical potentials close to oxygen release.

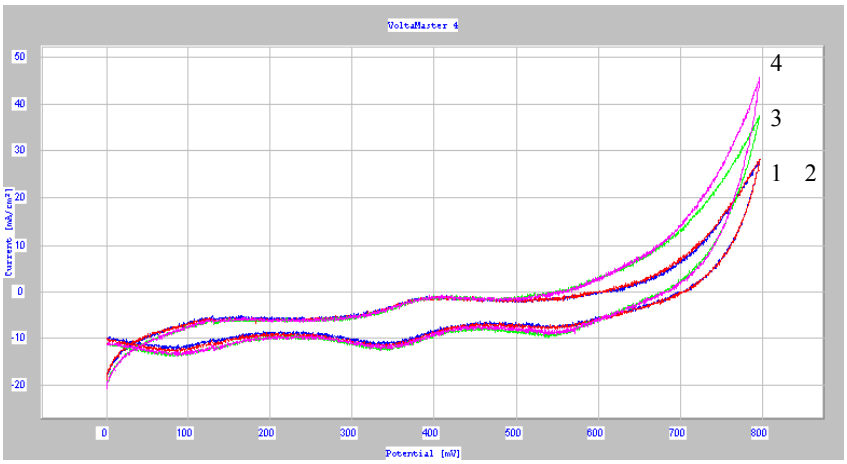

Figure 2. Cyclic voltammograms at different concentration (M) of Q: 0(1); $1.18 \cdot 10^{-2}$ (2); $2.04 \cdot 10^{-2}$ (3); $2.61 \cdot 10^{-2}$ (4) M; [KOH] = 5%; $6 \cdot 10^{-2}$ M Mn(VII); 25ºC.

Increasing the concentration of Q does not affect the peaks observed in curve 1 (in figure 2), in the absence of Q, but leads to oxygen release depolarisation. The depolarisation increase is greater with the concentration value of Q. This behaviour is different from the one observed on the nickel and platinum electrode where the effect of Q in the electrolyte solution was similar to the addition of Mn(VII) in the system [11,13]. This behaviour could be explained by the fact that the oxidation of Q takes place simultaneously with the O_2 release.

The temperature effect in the presence of Q is shown in figure 3.

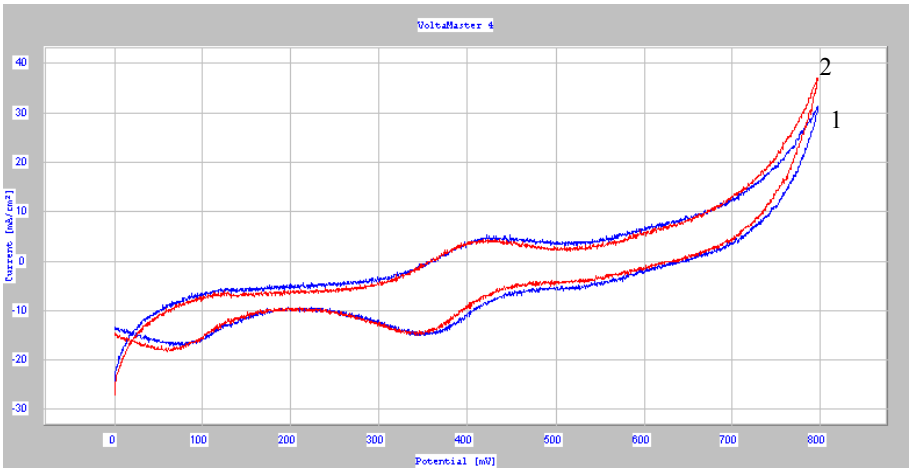

Figure 3. Cyclic voltammograms on the copper electrode at $3.8 \cdot 10^{-2}$M $KMnO_4$; 10% KOH solution; $2.61 \cdot 10^{-2}$M Q; temperature: 1)- 25°C, 2)- 40°C.

The effect of temperature increase on the peaks is insignificant (very low). On the other hand the oxygen release is slightly moved towards more negative potentials (figure 3).

Based on the results from cyclic voltammograms we made a laboratory electrolyser with perforated copper plate anode, used for the electrochemical regeneration of potassium permanganate.

Results obtained on this electrolyser are shown in table 3, where: Q – *electricity quantity;* U_{med} *- cell tension;* m_{Qi} *– initial quantity of quinoxaline;* m_{Qf} *– final quantity of quinoxaline; Conv.- conversion of quinoxaline* and m_{K2PDCA} *- K_2PDCA quantity.*

One can deduce, from table 3, that quinoxaline oxidation leads to **K_2PDCA** formation. Current efficiencies have values between 37 and 80% and substance efficiencies between 43 and 72%. In these conditions specific energy consumptions are between 4.8 and 17 KWh/kg K_2PDCA.

Table 3. Results from Mn(VII) regeneration process on the copper anode.

Nr. crt.	I [A]	i [A/m^2]	Q [C]	U_{med} [V]	T [°C]	m_{Qi} [g]	m_{Qf} [g]	Conv [%]	m_{K_2PDCA} [g]	η_s [%]	η_c [%]	C. En. Kwh/kg
1.	2	3.5	32400	2.9	45	2	0.2	90	2.7	71.9	52.73	9.67
2.	1	1.7	30000	2.5	35	2	0.34	83	2	53.3	42.19	10.42
3.	2	3.5	15000	3.1	35	1	0.4	60	1.3	69.3	54.84	9.94
4.	1	1.7	15000	2.2	45	2	1	50	1.88	50.1	79.31	4.88

- KOH concentration, % - 16.6
- Quinoxaline concentration, % – 1.4 – 2.8
- Mn(VII) concentration, % - 1.4.

The best performances – current efficiencies of ~55% and substance efficiencies up to 72% - are achieved at a current density of 3.5 A/dm^2 and maximum 90% conversions. Doubling the current density value leads to a significant decrease in current efficiency – down to 37%.

This behaviour could be explained by the simultaneous oxygen release and Mn(VII) regeneration, favoured by the high anodic potential and leading to current consumption for a secondary product – oxygen generation.

CONCLUSIONS

Mn(VII) regeneration, from Mn(VI) resulted after the Q oxidation chemical process, takes place on the copper electrode. We did not identify any investigation of such a process in the scientific literature. The best results – maximum current and substance efficiency and minimum specific energy consumption – are achieved at a current density of 3,5 A/dm^2 and the temperature interval 35 - 45°C.

High current efficiencies are achieved at small Q conversions.

High conversions and substance efficiencies are achieved at small current efficiencies. Instead, the extraction and separation of unreacted Q is no longer necessary.

Temperature has no significant effect in the studied interval.

EXPERIMENTAL SECTION

Cyclic voltammetry method

For the cyclic voltammetry studies we used a PGZ 301 Dynamic-EIS Voltammetry potentiostat with VoltaMaster 4 software manufactured by Radiometer Copenhagen and an electrolysis cell equipped with three electrodes:

- the working electrode – copper wire (0.031 cm^2)
- the counter electrode – platinum (0.25 cm^2)
- the reference electrode – Saturated Calomel Electrode.

All electrochemical potentials from this paper are related to the SCE electrode unless otherwise specified.

Electrolyte

The Mn(VII) regeneration process was studied by cyclic voltammetry at various concentrations of KOH (2 and 4M), K_2MnO_4 ($0.4\text{-}16\cdot10^{-3}$M) and quinoxaline ($1.18\text{-}3.62\cdot10^{-2}$M). Studies were carried out at three temperatures: 20, 45 and 55°C.

The KOH was delivered by Lach-Ner, quinoxaline was taken from Merck, $KMnO_4$ was a Riedel-de Haen product and K_2MnO_4 was synthesised in our laboratory.

The method for synthesizing potassium manganate is as follows: an alkaline aqueous solution of 8N KOH containing 10g of potassium permanganate was heated at a temperature of 120 °C. After the colour changed from violet (Mn(VII)) to intense green (Mn(VI)) the supersaturated solution of Mn(VI) was obtained. K_2MnO_4 crystals were filtered from this solution on a *S4* frit, washed with $CHCl_3$, dried and weighed, and then directly dissolved in 8N KOH solution (25 ml gauge flask) and used in cyclic voltammetry tests.

Laboratory electrolyser

In order to establish the current and substance efficiencies as well as the specific energy consumption for the pyrazine-2,3-dicarboxilic acid potassium salt (K_2PDCA), experiments were performed using the perforated copper plate anode.

The amount of electric current used in synthesis was correlated with the amount of quinoxaline in the electrolyte solution and the KOH concentration was properly chosen to ensure the required quantity for K_2PDCA formation as well as the alkaline environment for the Mn(VII) regeneration reaction in optimum conditions. The anode was manufactured from a 0.5 mm thick perforated copper plate – for ensuring the easy access of the solution on the two faces of the electrode (figure 4). Before the experiments the electrode was pickled in nitric acid and after each synthesis was treated in a mixture of sulphuric and oxalic acid.

Figure 4. Copper anode.

The ***general characteristics*** of the electrolyser are the following:

- Anodic surface, dm^2 – 0.56
- Cathodic surface, dm^2 – 0.034
- Sa/Sc ratio – 16.6
- Electrolyte volume, ml – 90
- Total volume of the electrolyser, ml – 150
- Current density, A/dm^2 – 3.5
- Working temperature, ^oC – 35-45
- Anodic material – perforated copper plate
- Cathodic material – stainless steel.

ACKNOWLEDGMENTS

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