Effect of some factors on the electrolysis production of sodium perchlorate from sodium chlorate using PbO_2/Pb-Ti electrode

Nguyen Ba Ngoc*

Institute of Technology, General Department of Defense Industry, 3 Cau Vong, Dong Ngac, Hanoi, Vietnam.
*Corresponding author: nguyenbangocvcn@gmail.com

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ABSTRACT

The electrolysis process of sodium perchlorate production from sodium chlorate using PbO_2/Pb-Ti electrode was studied by linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS) and electrolysis efficiency evaluation. The results showed that the technological parameters (sodium chlorate concentration, temperature, electrolyte current density, additive content and pH) strongly affected the polarization, charge transfer resistance and electrolysis efficiency. Therefore, the appropriate technological mode for the electrolysis process was selected as: $NaClO_3$ concentration 300 - 600 g/L; temperature 50 ^oC; current density 0.15 - 0.2 A/cm^2; NaF additive concentration 1-2 g/L; solution pH 7.

Keywords: Sodium perchlorate; Electrolysis; Sodium chlorate; PbO_2 electrode.

1. INTRODUCTION

Sodium perchlorate ($NaClO_4$) is considered the most important compound among perchlorates [1] because it is a precursor for the manufacture of main components (NH_4ClO_4, $LiClO_4$, $KClO_4$) in explosives, solid fuels, pyrotechnics, fireworks and other compounds. The safe and economical method for manufacturing $NaClO_4$ is electrolytic oxidation of sodium chlorate ($NaClO_3$) followed by crystallization. In which the positive electrode and electrolysis conditions (concentration of reactants, electrolysis current density, solution pH, temperature, type and content of additives) play an important role in the oxidation capacity of $NaClO_3$, electrolysis efficiency, power consumption, and product purity during the electrolysis process. Generally, the efficiency of the electrochemical process depends on the initial concentration of the raw materials [2, 3]. In most cases, high concentrations of reactants are used to avoid mass transfer limitations. Higher current densities can increase the rate of perchlorate production, but excessive current can lead to electrode degradation or side reactions. Elevated temperatures are often used to improve reaction kinetics, however, the temperature needs to be controlled to avoid unwanted side reactions. Maintaining a slightly acidic pH (e.g., below 9) is often preferred for efficient perchlorate formation. Some additives, such as sodium dichromate (for Pt anodes) and sodium fluoride (for lead dioxide anodes), are also used to improve the electrolysis performance [2, 4]. The choice of electrode material is crucial, as different materials have varying overpotentials for the desired reactions. Common types of positive electrodes that have been studied and used are magnetite, mixed metal oxide, graphite, diamond, Pt, PbO_2 [2-10]. The PbO_2 electrode shows the advantages of low oxidation potential of $NaClO_3$, high cumulative efficiency (50 - 70%), stability and cost savings [11-14]. This electrode is usually fabricated through a complex and costly process by chemically coating PbO_2 on a titanium or carbon substrate. This paper proposes a simple electrochemically produced titanium-based PbO_2 electrode and studies the influence of some technological factors on the electrolysis process of $NaClO_4$ production on this electrode.

2. EXPERIMENT

2.1. Materials and chemicals

Chemicals $NaClO_3$, NaOH, $Pb(NO_3)_2$, H_3BO_3, HNO_3, HF, NaF, Na_2SO_4 are chemicals used for analysis (Origin: China).

2.2. Prepare PbO_2/Pb-Ti electrode

The working electrodes for electrochemical measurements and the positive electrode (anode) for the electrolytic cell are made from titanium plates with active surface areas after finishing of 1 cm^2 and 200 cm^2 respectively, through the following stages: (i) Cutting the electrode blanks from 1 mm thick flat titanium plates; (ii) Degreasing in alkaline solution, activating in a mixed solution of HNO_3 and HF, and plating $50^{\pm3}$ µm thick lead (measured by micrometer) in a fluoroborate solution; (iii) Electrolysis to create a stable brown PbO_2 film in 20% Na_2SO_4 solution with a current density of 1 A/dm^2, temperature 25 ºC, time 3 hours [15]; (iv) The inactive surface parts of the electrodes are sealed with epoxy glue.

The counter electrode in electrochemical measurements and the negative electrode in the electrolytic cell were made from SUS 304 stretched mesh, measuring 100 × 100 × 1.5 (mm).

2.3. Electrochemical measurements

Electrochemical measurements were carried out on a Zennium Pro apparatus (Zahner – Germany) using a three-electrode system. The working electrode and the counter electrode were a PbO_2/Pb-Ti electrode and SUS 304 expanded mesh, respectively, fabricated as in section 2.2. The reference electrode was an Ag/AgCl electrode.

Polarization measurements were carried out at a linear potential sweep rate of 1 mV/s, ranging from the equilibrium electrode potential to +2 V (Ag/AgCl) in electrolyte solutions with compositions and temperatures as shown in table 1.

Electrochemical impedance measurements were carried out at equilibrium potential, amplitude of 5 mV, frequency range from 10 kHz to 50 mHz in electrolyte solutions with compositions and temperatures as shown in table 1.

2.4. Evaluation of electrolysis efficiency

To evaluate the effect of technological parameters on electrolysis efficiency, electrolysis was carried out with a PbO_2/Pb-Ti anode electrode and a SUS 304 cathode plate fabricated as described in section 2.2. The solution composition and electrolysis mode to evaluate each parameter are specified in section 2.5. The electrode assembly and electrolysis cell are shown in figure 1, in which the volume of the studied electrolysis solution is 2 liters.

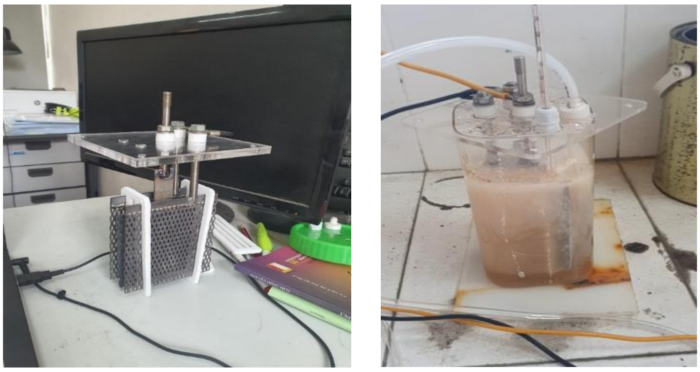


Figure 1. *Electrode pair and test electrolytic cell.*

The electrolysis efficiency of producing $NaClO_4$ from $NaClO_3$ is calculated using the following formula:

$$H(\%) = \frac{m_{tt}}{m_{lt}} = \frac{\left(C_0 - C_f\right) \times V \times n \times F}{A \times i \times S \times 3600 \times t} \times 100\% \qquad (1)$$

Here: H (%) is the efficiency of $NaClO_3$ electrolysis current; C_0 (g/L) and C_f (g/L) are the initial and final $NaClO_3$ concentrations (determined by ion liquid chromatography according to TCVN

6494-4 : 2000) of the electrolysis solution, respectively; V (L) is the volume of the electrolysis cell, V = 2 liters; n is the number of electrons exchanged, n = 2; F is the Faraday constant, 96500 C/mol; A is the molar mass of $NaClO_3$, A = 106.44 g/mol; i (A/cm^2) is the electrolysis current density; S (cm^2) is the area of the PbO_2/Pb-Ti electrode, S = 200 cm^2 and t (hours) is the electrolysis time.

2.5. Study on the influence of some technological parameters

The effects of some technological parameters, including initial concentration of $NaClO_3$ (C_0 – g/L), temperature, anode current density, C_{NaF} additive concentration and solution pH on the electrolysis process were studied by evaluating the current efficiency in the corresponding solution components and electrolysis modes as shown in table 1; combined with electrochemical measurement methods in the corresponding solutions.

Table 1. *Solution composition and electrolysis mode for the study.*

Technology parameters	**Electrolyte solution composition**			**Electrolysis technology mode**		
	C_0 (g/l)	***C_{NaF} (g/L)***	***pH***	***i_A (A/cm^2)***	***Time (hours)***	***Temperature (^oC)***
Initial concentration of $NaClO_3$	750	0	7	-	-	30
	600	0	7	0.15	6	30
	450	0	7	-	-	30
	300	0	7	0.15	4	30
	150	0	7	0.15	4	30
Temperature	600	0	7	0.15	6	30
	600	0	7	0.15	6	50
	600	0	7	0.15	6	70
Electrolytic current density	600	0	7	0.05	18	50
	600	0	7	0.10	9	50
	600	0	7	0.15	6	50
	600	0	7	0.20	4.5	50
	600	0	7	0.25	3.6	50
Additive content	600	0	7	0.15	6	50
	600	1	7	0.15	6	50
	600	2	7	0.15	6	50
	600	2	7	0.15	13	50
pH	600	2	5	0.15	13	50
	600	2	7	0.15	13	50
	600	2	9	0.15	13	50

3. RESULTS AND DISCUSSION

3.1. Effect of concentration $NaClO_3$

Figure 2 shows the anodic polarization curves of the PbO_2/Pb-Ti electrode in the range from the equilibrium potential E_0 to + 2.0 V (Ag/AgCl) at 30 °C in a solution with a $NaClO_3$ concentration of 150 – 750 g/L. It can be seen that as the $NaClO_3$ concentration increases in the solution from 150 to 450 g/L, the polarization curve shifts toward a more negative potential. This is the result of a decrease in concentration polarization due to an increase in the concentration of the reactant. However, as the $NaClO_3$ concentration continues to increase from 450 to 750 g/L, the polarization curve shifts toward a more positive potential. This result is because when the $NaClO_3$ concentration in the solution increases (exceeding 450 g/L), the diffusion of the reaction product ($NaClO_4$) from the electrode surface into the solution becomes more difficult. From figure 2, it can also be inferred that, in the electrolysis process of producing $NaClO_4$ from $NaClO_3$ on PbO_2/Pb-Ti electrode, the electrolysis process should start and end at the initial and final concentrations of $NaClO_3$ of 600 g/L and 300 g/L, respectively, to ensure energy saving.

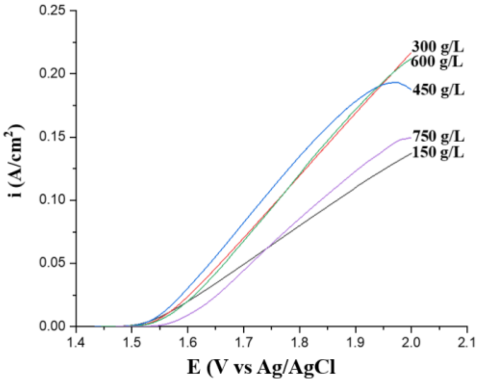
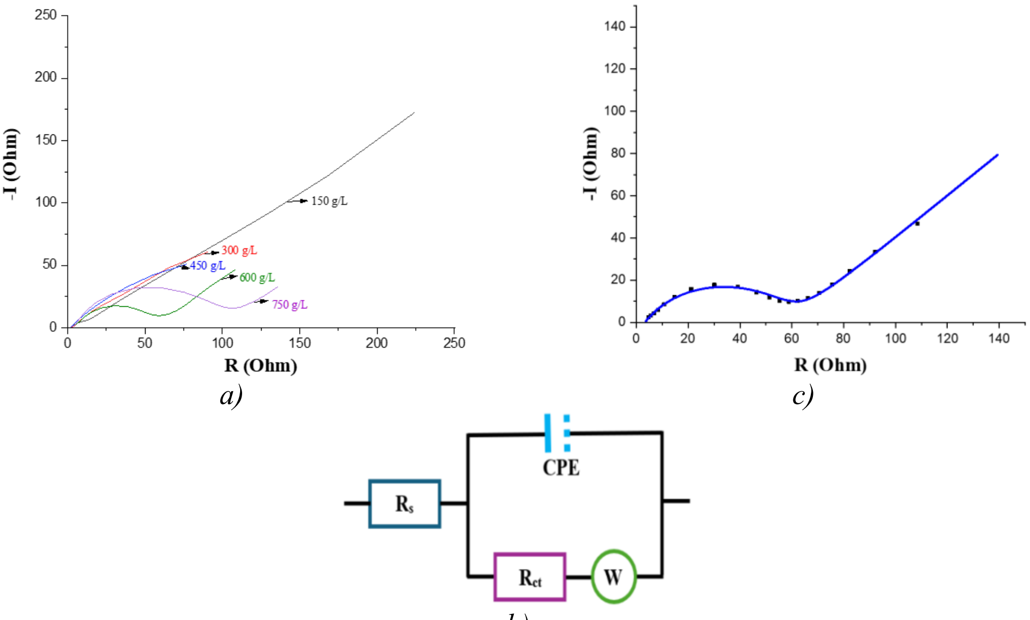


Figure 2. *Anode polarization curve on PbO_2/Pb-Ti electrode in the potential range from E_0 to +2.0 V (Ag/AgCl) at 30 °C in a solution with a $NaClO_3$ concentration of 150 – 750 g/L.*



a)

c)

b)

Figure 3. *Electrochemical impedance spectra of PbO_2/Pb-Ti electrode at equilibrium potential in electrolyte solutions with $NaClO_3$ concentrations from 150 g/L to 750 g/L (a); equivalent electrochemical circuit (b) and simulated impedance spectrum of the equivalent circuit with the impedance spectrum measured at $NaClO_3$ concentration of 600 g/L (c).*

Figure 3a shows the electrochemical impedance spectrum of the PbO_2/Pb-Ti electrode at the equilibrium potential E_0, temperature 30 °C, potential amplitude 5 mV, frequency range from 10 kHz to 30 mHz, in a solution with $NaClO_3$ concentration from 150 – 750 g/L. Figure 3b is the equivalent circuit used to simulate the electrochemical process occurring on the PbO_2/Pb-Ti electrode. In which Rs (Ω) is the resistive element, representing the solution resistance. CPE is the constant phase element, representing the capacitance of the electric double layer, Rct (Ω) is the resistive element, representing the charge transfer resistance. W is the Warburg impedance, representing the diffusion layer impedance. Figure 3c shows the simulated impedance curve (solid line) obtained by fitting the equivalent circuit of figure 3b to the actual impedance curve measured at a $NaClO_3$ concentration of 600 g/L (discontinuous square dotted line).

The simulated impedance spectrum is relatively similar to the measured impedance curve with a fitting error of 4.9%, showing that the equivalent circuit in figure 3b simulates well the electrochemical process occurring on the PbO_2/Pb-Ti electrode. The electrochemical parameters obtained from fitting the equivalent circuit to the impedance spectrum in figure 3a are shown in table 2. In the measurement, C_{dl} (μF) is the double-layer capacitance and σ_w is the Warburg coefficient. It can be seen that the resistance of the electrolyte solution reaches its minimum value at a $NaClO_3$ concentration of 600 g/L. The charge transfer resistance gradually decreases when the $NaClO_3$ concentration increases to 450 g/L and then gradually increases when the reactant concentration continues to increase. The variation of the Warburg coefficient shows that the $NaClO_3$ concentration of 450 g/L is the most favorable for the diffusion of reactants and reaction products into/out of the electrode surface.

***Table 2.** Effect of $NaClO_3$ concentration on electrochemical parameters.*

Concentration of $NaClO_3$ (g/L)	**Electrochemical parameters**			
	R_s (Ω)	R_{ct} (Ω)	C_{dl} (μF)	σ_w (DW)
150	*1.425*	*73.89*	*26.9*	*413.9*
300	*1.332*	*3.041*	*20.9*	*78.82*
450	*1.329*	*1.108*	*0.278*	*40.22*
600	*1.313*	*57.88*	*14.99*	*48.11*
750	*1.367*	*103.2*	*29.36*	*79.08*

Table 3 shows the change in current efficiency when electrolysis is carried out at 30 °C, anode current density of 0.15 A/cm^2, pH 7, with initial $NaClO_3$ concentrations in the solution of 150, 300, 600 g/L, respectively. It can be seen that the efficiency of the electrolysis process gradually decreases as the electrolysis concentration range of $NaClO_3$ decreases. In particular, at the low concentration range (starting at 150 g/L and ending at 45.5 g/L), the efficiency of the electrolysis process decreases sharply to only 43.9%.

***Table 3.** Effect of $NaClO_3$ concentration on electrolysis efficiency.*

No.	**Initial concentration of $NaClO_3$, g/l**	**Final concentration of $NaClO_3$, g/l**	**Electrolysis efficiency, %**
1	600	326	76,7
2	300	151	68,2
3	150	45,5	43,9

3.2. Effect of temperature on electrolysis

Figure 4 is the impedance spectra on the PbO_2/Pb-Ti electrode obtained in an electrolyte solution with a $NaClO_3$ concentration of 600 g/L at an equilibrium electrode potential, a potential amplitude of 5 mV, a frequency range from 10 kHz to 30 mHz, with temperatures of 30, 50 and 70 °C. The electrochemical parameters obtained by fitting the measured results to the equivalent circuit of figure 3b are shown in table 4. It is found that at 50 °C, the electrolysis process has the smallest charge transfer resistance and diffusion resistance.

Table 5 shows the change in current efficiency when electrolysis is carried out at an anode current density of 0.3 A/cm^2, time of 6 hours, pH 7, initial $NaClO_3$ concentration in the solution of 600 g/L, with temperatures of 30, 50 and 70 °C, respectively. It is found that, when the electrolysis temperature increases, the current efficiency decreases. This can be explained by the fact that increasing the electrolysis temperature makes the oxygen escape process more favorable. However, increasing the solution temperature to 50 °C will reduce the power consumption due to the reduction of solution resistance, charge transfer resistance and diffusion resistance (as seen in table 4) without much decrease in electrolysis efficiency (-4.2%). Therefore, the temperature of 50 °C is suitable for the electrolysis process.

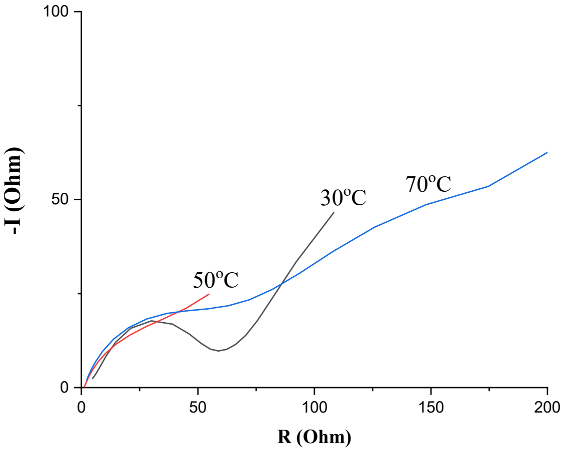


Figure 4. *Electrochemical impedance spectra of PbO_2/Pb-Ti electrode at equilibrium potential at different electrolyte solution temperatures.*

Table 4. *Effect of electrolysis temperature on electrochemical parameters.*

Temperature (°C)	**Electrochemical parameters**			
	R_s (Ω)	R_{ct} (Ω)	C_{dl} (µF)	σ_W (DW)
30	*1.313*	*57.88*	*14.99*	*28.11*
50	*1.073*	*56.12*	*12.9*	*9.663*
70	*1.065*	*89.16*	*15.33*	*54.61*

Table 5. *Effect of temperature on electrolysis efficiency.*

No.	**Initial concentration of $NaClO_3$, g/l**	**Final concentration of $NaClO_3$, g/l**	**Temperature, °C**	**Electrolysis efficiency, %**
1	600	326	30	76.7
2	600	341	50	72.5
3	600	354	70	68.8

3.3. Effect of electrolysis current density

Table 6 shows the change in current efficiency when electrolysis is carried out in a solution with an initial concentration of $NaClO_3$ of 600 g/L, temperature of 50 °C, solution pH of 7, with current densities of 0.05, 0.1, 0.15, 0.2 and 0.25 A/cm^2, respectively. As the electrolysis current density increases, the electrolysis efficiency increases. However, in the current density range from 0.15 to 0.2 A/cm^2, when the current density increases, the efficiency does not increase much. Even when the current density increases to 0.25 A/cm^2, the electrolysis efficiency decreases slightly. This is explained by the fact that the electrolysis process of producing $NaClO_4$ from $NaClO_3$ is always accompanied by a side reaction of releasing oxygen. When the electrolysis current density increases, the proportion of current devoted to the oxidation of $NaClO_3$ increases, leading to an increase in electrolysis efficiency. However, due to the limitation of reactant concentration and diffusion limit, when increasing the electrolysis current density beyond a certain value, the partial current for $NaClO_3$ oxidation does not increase. At that time, increasing the current density only increases the current ratio of the oxygen gas release process, leading to a decrease in electrolysis efficiency. On the other hand, when electrolysis occurs at high current density, the gas release process occurs strongly, increasing the risk of destroying the porous electrode. From the above results, it can be seen that the appropriate electrolysis current density for $NaClO_3$ electrolysis is 0.15 - 0.2 A/cm^2.

Table 6. *Effect of current density on electrolysis efficiency.*

No.	Initial concentration of $NaClO_3$, g/l	Final concentration of $NaClO_3$, g/l	Current density, (A/cm^2)	Electrolysis efficiency, %
1	600	394	0.05	57.6
2	600	360	0.10	67.2
3	600	341	0.15	72.5
4	600	338	0.20	73.3
5	600	339	0.25	73.0

3.4. Effects of additives

Table 7 shows the change in current efficiency when electrolysis is carried out at an anode current density of 0.15 A/cm^2, pH 7, initial $NaClO_3$ concentration of 600 g/L, temperature of 50 °C, in solutions without and with 1 and 2 g/L of NaF additive, respectively. It is found that the presence of NaF additive with concentrations of 1 and 2 g/L increases the electrolysis efficiency by 1.1 and 5.6%, respectively. In particular, with a NaF additive concentration of 2 g/L, the electrolysis efficiency is still maintained at 71.7% even when electrolysis is performed in the low $NaClO_3$ concentration range (down to 45 g/L). The effect of increasing the electrolysis efficiency of NaF can be explained by the adsorption of F^- ions on the electrode surface, increasing the oxygen release potential and thus improving the current fraction for $NaClO_3$ oxidation. The ability to maintain high electrolysis efficiency of PbO_2/Pb-Ti electrode with NaF additive at low concentration of reactant shows similarity with other types of PbO_2 electrodes [7] that have been studied and manufactured. This shows the prospect of applying this electrode to a practical electrolysis process.

Table 7. *Effect of additives on electrolysis efficiency.*

No.	Initial concentration of $NaClO_3$, g/l	Final concentration of $NaClO_3$, g/l	Additive concentration NaF, g/l	Electrolysis efficiency,%
1	600	341	0	72.5
2	600	317	1	73.6
3	600	321	2	78.1
4	600	45	2	71.7

3.5. Effect of pH on electrolysis

Table 8 shows the change in current efficiency when electrolysis was carried out at an anode current density of 0.15 A/cm^2, time of 6 hours, initial $NaClO_3$ concentration in solution of 600 g/L, temperature of 50 °C, NaF concentration of 2 g/L, with solution pH of 5, 7 and 9, respectively. It can be seen that the current efficiency was highest at the neutral level and decreased further at the alkaline level. On the other hand, when electrolysis was performed at a pH of 9, the solution became cloudy with suspended yellow-brown solids, possibly due to anode corrosion. Therefore, pH 7 was chosen for the electrolysis process.

Table 8. *Effect of solution pH on electrolysis efficiency.*

No.	Initial concentration of $NaClO_3$, g/l	Final concentration of $NaClO_3$, g/l	pH	Electrolysis efficiency,%
1	600	65	5	69.1
2	600	45	7	71.7
3	600	91	9	65.7

4. CONCLUSIONS

Depending on the results of this study, the following conclusions can be drawn:

i) Technological factors (concentration of reactants, electrolysis current density, temperature, solution pH and additives) strongly affect the kinetic parameters as well as the efficiency of the electrolysis process to produce sodium perchlorate from sodium chlorate on PbO_2/Pb-Ti electrode. The appropriate electrolysis conditions obtained are: $NaClO_3$ concentration 300 – 600 g/L; temperature 50 °C; electrolysis current density 0.15 – 0.2 A/cm^2; NaF concentration 2 g/L; pH 7.

ii) PbO_2/Pb-Ti electrodes fabricated by the electrochemical method are promising for application in the practical electrolysis process of producing $NaClO_4$.

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TÓM TẮT

Ảnh hưởng của một số yếu tố tới quá trình điện phân chế tạo natri perchrorate từ natri chlorat sử dụng điện cực PbO_2/Pb-Ti

Quá trình điện phân chế tạo natri perchlorate từ natri chlorate sử dụng điện cực PbO_2/Pb-Ti đã được nghiên cứu bằng phương pháp quét thế tuyến tính (LSV), phổ tổng trở điện hóa (EIS) và đánh giá hiệu suất điện phân. Kết quả cho thấy các thông số công nghệ (nồng độ natri chlorate, nhiệt độ, mật độ dòng điện phân, hàm lượng phụ gia và pH) ảnh hưởng mạnh đến sự phân cực, điện trở chuyển điện tích và hiệu suất điện phân. Từ đó, chế độ công nghệ thích hợp cho quá trình điện phân được lựa chọn là: nồng độ $NaClO_3$ 300 – 600 g/L; nhiệt độ 50°C; mật độ dòng điện 0,15 - 0,2 A/cm^3; nồng độ phụ gia NaF 1-2 g/L; pH dung dịch 7.

Từ khóa: Natri perchlorate; Điện phân; Natri chrorate; Điện cực PbO_2.