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STUDYING THE ELECTROCHEMICAL BEHAVIOUR OF RED PHOSPHORUS IN HYDROCHLORIC ACID SOLUTION

Abstract

Elemental phosphorus is an interesting subject for electrochemical research. Situated in the middle of the third period, it exhibits equal capacity for both oxidation and reduction reactions. This paper presents the results of a study of the oxidation reaction of red phosphorus using a composite phosphorus-graphite electrode in a hydrochloric acid solution under galvanostatic conditions. The influence of key electrochemical parameters, such as current density and electrolyte concentration, on the phosphorus oxidation current efficiency was studied. Optimal conditions for the oxidation process were determined. It was shown that in the presence of chloride ions, competitive anodic formation of active chlorine occurs, significantly affecting the mechanism and products of phosphorus oxidation. The obtained study results demonstrate that, during anodic polarization, elemental phosphorus in aqueous solutions is directly oxidized to form hypophosphite-, phosphite-, and phosphate-ions.

Keywords: phosphorus production, elemental phosphorus, composite electrode, electrolysis, chloride-ions, catalyst, phosphorus compounds

Introduction

Phosphorus sludge is formed during the condensation of yellow phosphorus, as a result of incomplete purification of the exhaust dust and gas components [1]. It is known that sludges with a phosphorus content of at least 45-50% are processed into thermal phosphoric acid by incineration in cyclone apparatuses. However, during sludge incineration, slag is formed from the mineral portion of the sludge, which is a secondary waste, and the resulting acid contains suspended solids and lower forms of phosphorus [2,3].

Therefore, the aim of this research was to develop a rational and cost-effective technical solution that would maximize the recycling of phosphorus production waste and by-products, yielding environmentally safe end products.

This research focuses on a specific approach to studying the electrochemical properties of elemental phosphoru in aqueous solutions. This method is used to develop approaches to utilization phosphorus production waste and producing environmentally friendly phosphorus-containing compounds.

The novelty lies in the fact that, as a result of studying the anodic oxidation of elemental phosphorus, electrochemical methods for the neutralization of phosphorus production waste were developed for the first time.

Materials and Methods

Experimental part

To study the electrochemical oxidation of elemental white phosphorus, electrolysis was carried out under galvanostatic conditions. Phosphorus-graphite electrodes were used as the anode, and a graphite rod was used as the cathode. The experiments were carried out in a glass cell, with the anode-cathode space separated by an MK-40 cation exchange membrane. A rectifier DSPS-305DM served as the current source. A schematic diagram of the setup is presented in [4]. Solutions of various concentrations in the range of 0.25–1.25 mol/l were used as the electrolyte.

All experiments were carried out on a phosphorus-graphite electrode with a phosphorus content of 50.0% by mass. Electrolysis was carried out in a 100 cm^3 vessel equipped with a water jacket for cooling. The duration of electrolysis was considered in the range from 0.25 to 1.0 hours. Quantitative analysis was performed on the products of single oxidation of phosphorus of varying degrees of oxidation that had passed into the solution, hypophosphite ions P(+1) by permanganometric method, phosphite ions P(+3) by iodometric method, and phosphate ions P(+5) by the method of I.P. Moizhe's photometric method [5,6].

Results and discussion

Based on the values of standard potentials [7], the following reactions may occur on the surface of the electrode when the phosphorus is polarized:

$$P + 2\,H_2O \rightarrow H_3\,PO_2 + H^+ + e \qquad E^0 = -\,0{,}511\ B \qquad (1)$$

$$P_{(white)} + 3\,H_2O \rightarrow H_3PO_3 + 3H^+ + 3e \qquad E^0 = -\,0{,}502B \qquad (2)$$

$$P_{(white)} + 4\,H_2O \rightarrow H_3PO_4 + 5H^+ + 5e \qquad E^0 = -\,0{,}411B \qquad (3)$$

To study the anodic oxidation of elemental phosphorus in chloride solutions, the influence of hydrochloric acid concentration, current density, and electrolysis duration on the current efficiency of phosphorus oxidation was investigated.

The anodic oxidation of phosphorus in chloride solutions can be explained as follows: at a certain polarisation, chlorine is released on the graphite electrode according to the reaction (4).

The chlorine released at the anode partially dissolves in the electrolyte and is hydrolysed according to the reaction:

$$Cl_2 + H_2O \rightarrow HClO + HCl \qquad (4)$$

Reaction equilibrium constant:

$$K = \frac{[H^+]\cdot[Cl^-]\cdot[HClO]}{[Cl_2]}$$

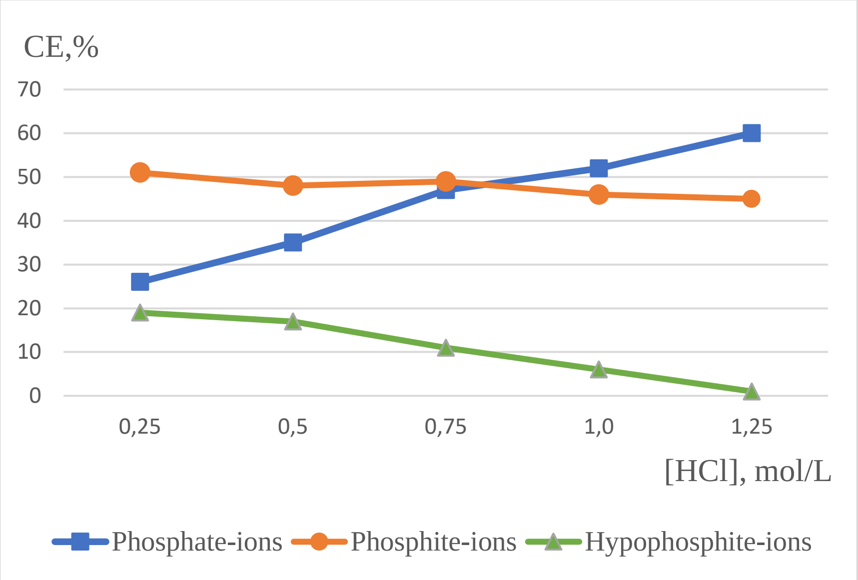
at 25°C is $3.9\cdot10^{-4}$. With an increase in the concentration of chlorine and hydrogen ions, the equilibrium concentration of hypochlorous acid decreases. Thus, the phosphorus-graphite electrode in the anode space of the electrolyser can be oxidised with chlorine and hypochlorous acid according to the following reactions:

$$2P + 5Cl_2 + 8H_2O \rightarrow 3H_3\,PO_4 + 10\,HCl \qquad (5)$$

$$P + 4HClO \rightarrow PO_4^{3-} + 4H^+ + 4Cl \qquad (6)$$

In which, as can be seen, chlorine ions are formed again, i.e. the process proceeds catalytically. This is evidenced by the results of the experimental data obtained.

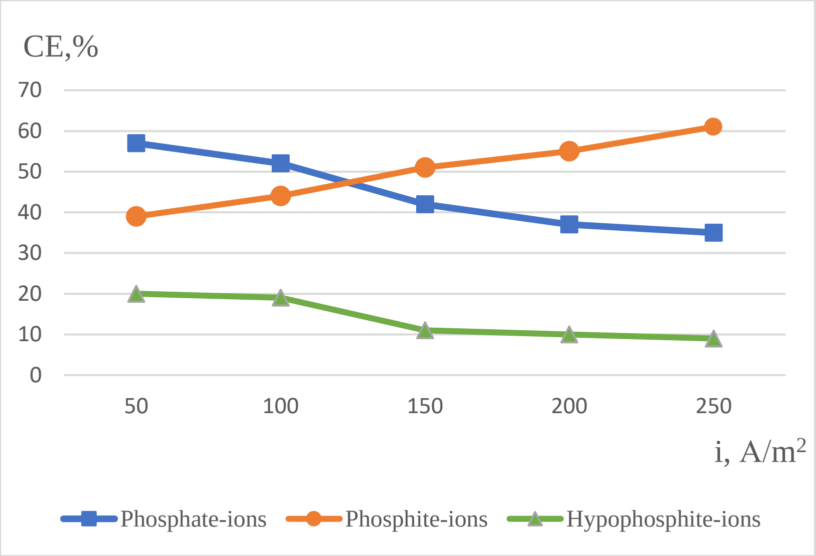
An increase in the concentration of the hydrochloric acid solution has a positive effect on the oxidation current efficiency of elemental phosphorus (Figure 1). Electrolysis was carried out at a current density of 100 A/m² and electrolysis duration of 0.25 hours. The maximum oxidation rate of elemental phosphorus is reached at [HCl] = 1.25 mol/L, and the current efficiency of phosphate-ion formation is 60%, i.e. the phosphate- and hypophosphite-ions formed in the solution have time to oxidise to phosphate-ions. We assume that the chloride-ions present in the solution have a catalytic effect and accelerate the oxidation process of elemental phosphorus. Thus, our assumptions are confirmed by the literature data.



τ - 0,25 hour; i – 100 A/m^2; C:P-50:50

Fig. 1. Effect of hydrochloric acid concentration on the current efficiency of phosphorus oxidation

The effect of current density on the anodic oxidation of elemental phosphorus is shown in Figure 2. Electrolysis conditions: electrolysis duration 0.25 hours, electrolyte concentration 1.0 mol/l. As the current density increases, the current efficiency of phosphate ion formation decreases from 57% to 35%. This is due to the fact that as the current density increases, the process of gaseous chlorine evolution at the anode intensifies and, as a result, the rate of active chlorine molarisation exceeds the rate of its interaction with phosphorus, and gaseous chlorine is removed from the sphere by the reaction (4).



[HCl]- 1,0 mol/L; τ-0,25; C:P –50:50

Fig.2. Effect of current density on the oxidation current efficiency of phosphorus in hydrochloric acid solution

The effect of electrolysis duration on the anodic oxidation of phosphorus in the range from 0,25 to 1,25 hours was also considered under conditions of 0.25 mol/L and 50 A/m^2. With an increase in the duration of electrolysis, the current efficiency of phosphate ion formation initially increases (up to 0,75 hours), but further increases in the duration of electrolysis lead to a significant decrease in current efficiency.

Conclusions

For the first time, the anodic oxidation of elemental phosphorus under galvanostatic conditions has been studied. The effects of current density and electrolyte concentration on the phosphorus oxidation current efficiency have been investigated. Under optimal conditions, the current efficiency of anodic oxidation of elemental phosphorus is 75% in HCl solutions. During a prolonged process, the concentration of discharging ions in the anode space decreases and the current efficiency of elemental phosphorus oxidation decreases. It is also visually observed that during prolonged electrolysis, the electrolyser heats up, which lead to the destruction of the electrode under study, since the melting point of white phosphorus is only 44%.

Thus, we have investigated the anodic oxidation of elemental white phosphorus for the first time and demonstrated the catalytic action of chloride ions on the anodic process.

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ТҰЗ ҚЫШҚЫЛЫ ЕРІТІНДІСІНДЕГІ ҚЫЗЫЛ ФОСФОРДЫҢ ЭЛЕКТРОХИМИЯЛЫҚ ӘРЕКЕТІН ЗЕРТТЕУ

Түйін

Элементті фосфор электрохимиялық зерттеулер үшін қызықты объект болып табылады. Үшінші периодтың ортасында орналасқан фосфор тотығу және тотықсыздану реакциялары үшін бірдей қабілеттілік көрсетеді. Ұсынылып отырған жұмыста, гальваностатикалық жағдайда тұз қышқылы ерітіндісінді композициялық фосфор-графит электродты пайдаланып, қызыл фосфордың тотығу реакциясын зерттеу нәтижелері берілген. Фосфордың тотығуының ток бойынша шығымына негізгі электрохимиялық параметрлердің: ток тығыздығы және электролит концентрациясының әсерлері зерттеледі. Тотығу процесінің тиімді жағдайлары анықталды. Хлорид иондарының қатысында, белсенді хлордың бәсекеге қабілетті анодты түзілуі орын алатындығы көрсетілді, ол фосфордың тотығу механизмі мен өнімдеріне айтарлықтай әсер етеді. Алынған нәтижелер негізінде анодты поляризация кезінде сулы ерітінділердегі элементті фосфордың гипофосфит-, фосфит- және фосфат-иондарын түзе отырып тікелей тотығатындығы көрсетілді.

Кілттік сөздер: фосфор өндірісі, элементтік фосфор, композиттік электрод, электролиз, хлорид иондары, катализатор, фосфор қосылыстары.

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ИЗУЧЕНИЕ ЭЛЕКТРОХИМИЧЕСКОГО ПОВЕДЕНИЯ КРАСНОГО ФОСФОРА В РАСТВОРЕ СОЛЯНОЙ КИСЛОТЫ

Аннотация

Элементарный фосфор является интересным объектом для электрохимических исследований. Находясь в середине третьего периода, он в равной мере проявляет способность к реакциям как окисления, так и восстановления. В этой работе приведены результаты исследования реакции окисления красного фосфора в виде композиционного фосфор-графитового электрода в солянокислом растворе в гальваностатических условиях. Изучены влияние основных электрохимических параметров такие как плотности тока, концентрации электролита на выход по току окисления фосфора. Определны оптимальные условаия процесса окисления. Показано, что в присутствии хлорид-ионов происходит конкурентное анодное образование активного хлора, что существенно влияет на механизм и продукты окисления фосфора. По полученным результатам исследования, показано, что при анодной поляризации элементраный фосфор в водных растворах непосредственно окисляется с образованием гипофосфит-, фосфит- и фосфат-ионов.

Ключевые слова: производство фосфора, элементарный фосфор, композитный электрод, электролиз, хлорид-ионы, катализатор, соединения фосфора.