



A potentiometric phosphate ion sensor based on electrochemically modified nickel electrode

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ABSTRACT

The effective detection of phosphate ions is very important in the fields of chemistry, biology, medicine, environment and industry. At present, the detection of phosphate ion mainly depends on molybdenum blue colorimetry. Although this method is accurate, it needs sample pretreatment, complex operation and high cost. Therefore, it is urgent to design and develop a phosphate ion sensor with high efficiency, accuracy, simple operation and real-time on-line detection. In this study, a phosphate ion sensor was designed and developed by electrochemical modification based on nickel metal electrode. Nickel electrode was specifically modified to form a phosphate of Ni on the surface of Ni electrode. The phosphate ion response of Ni-PME(Nickel-phosphate modified electrode) was evaluated in a two-electrode system. The results show that under the condition of pH 4, Ni-PME can respond to phosphate ions with a concentration of 10^{-5} M to 0.1 M, the response slope is -81.0 mV dec^{-1} , and the selectivity coefficients for common anions are below -2 . The response time is less than 20 s. The stability of electrode potential is very high, and the fluctuation of 24-hour continuous test potential is within ± 3 mV. The lifetime is more than 4 weeks. Compared with the traditional molybdenum blue colorimetry, Ni-PME showed good accuracy and good recovery rate.

1. Introduction

Phosphorus is one of the important constituent elements of animals and plants. It is widely distributed in the biosphere. The detection of phosphorus is of great significance in the fields of industry, agriculture and environmental pollution prevention and control [1,2]. Phosphate is one of the natural ingredients of almost all foods. As an important food ingredient and functional additive, phosphate is widely used in food processing. In terms of environmental protection, in recent years, with the development of modern industry and agriculture, a large number of phosphorus containing pollutants have been discharged into natural water bodies, greatly increasing the content of nutrients in natural water bodies, making water bodies eutrophic, causing excessive growth of algae and some aquatic vegetation, which will greatly reduce the concentration of dissolved oxygen in water. Then it leads to the large-scale death of aquatic animals such as fish and shrimp, destroys the ecological balance of nature, and finally leads to a series of environmental problems. Accurately and dynamically monitoring the content of phosphate in water can timely monitor the water pollution in the region and

provide help for the pollution prevention and treatment of the natural environment. Therefore, using sensor technology to determine the content of phosphorus in water has very important practical significance in various fields such as industry, agriculture, environment and medicine.

At present, molybdenum ammonium blue spectrometry and high performance liquid chromatography(HPLC) are generally used for the detection of phosphate [3–6]. Although these two methods have high detection accuracy, they can not meet the actual needs of real-time online monitoring because of the complex pretreatment operation. The ion sensor has the advantages of fast, efficient, convenient and real-time monitoring. At present, there is no electrochemical phosphate ion sensor in the ion sensor market. The main "neck" technical difficulty in the research and development of phosphate ion sensor is that phosphoric acid is a ternary acid, which has three-stage dissociation in aqueous solution. The valence form and relative distribution proportion of phosphate are different under different pH conditions, which makes it very difficult to detect phosphate quantitatively.

In recent years, some research teams have reported a lot of research

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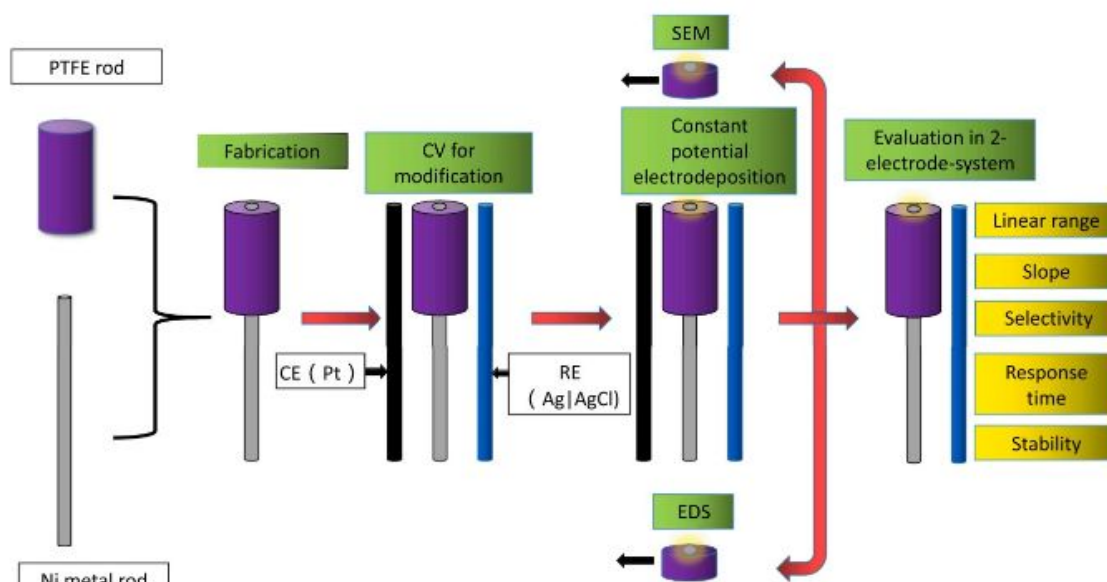
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Scheme 1. Fabrication, modification and evaluation of Ni-PME

progress on phosphate ion sensors. Many have developed a series of fluorescent spectral phosphate ion sensors based on the spectral characteristics of phosphate [7–14]. In terms of electrochemical sensors, cobalt is widely used in many phosphate sensors. Dan et al [15], proposed an all solid state phosphate ion sensor modified with cobalt phosphate on the surface of metal cobalt electrode, and revealed its response mechanism to three different valence phosphate at different pH. Meruva et al [16], clarified that the potential response of modified cobalt electrode to phosphate ion is a mixed potential response mechanism by CV and XPS based on the research of Dan et al. Kebin et al [17], made a more in-depth analysis of the electrochemical response mechanism of cobalt based phosphate ion sensor by using cyclic voltammetry and XRD in 2018, and established the actual detection standard curve based on different pH. Because the cobalt based sensor can only detect phosphate ions under weak acidic conditions, Kebin et al. used the surface doped phosphate complex technology to study the phosphate ion sensor based on molybdenum [18] and tungsten [19], which has good response ability to phosphate ions under weak alkaline conditions. In addition, cobalt ferroalloy [20] and silver [21] have also been used in the research of some phosphate ion sensors.

In this study, a potential electrochemical phosphate ion sensor with high efficiency, accuracy and simple operation is developed and designed. The response mechanism was studied by cyclic voltammetry, SEM and EDS.

2. Experimental

2.1. Materials and reagents

All chemicals were of analytical grade and used as received without further purification. All solutions were prepared with ultra pure water with a resistivity of 18.2 MΩ cm. Hydrogen phosphate disodium (Na_2HPO_4), sodium bicarbonate (NaHCO_3), sodium acetate (NaCOOH), sodium chloride (NaCl), sodium sulfate (Na_2SO_4), hydrochloric acid (HCl), and sodium hydroxide (NaOH) were purchased from Xinke, Shenyang, China. Nickel rods ($\varnothing 2 \text{ mm} \times 100 \text{ mm}$, 99.99%) and nickel plates ($0.1 \text{ mm} \times 50 \text{ mm} \times 50 \text{ mm}$) were obtained from Guantai Metal, Tianjin, China.

2.2. Apparatus

SEM was performed with a Quanta250-FEG field emission scanning

electron microscope (FEI, Czech) accompanied by energy-dispersive spectrometry. EDS was performed with an X-MAX-20 (Oxford, UK). Electrochemical measurements were carried out using a Versastat3 electrochemical workstation (Ametek, USA).

2.3. Preparation of the nickel electrode

At first, the surface of the nickel wire ($\varnothing 2 \text{ mm} \times 100 \text{ mm}$) was polished by sandpapers of #80, #240, and #1000 in turns for 1 min. It was then washed for 30 min using an ultrasonic cleaner. One end of the nickel wire was covered with a poly tetrafluoroethylene (PTFE, $\varnothing 10 \text{ mm} \times 20 \text{ mm}$) tube at one end as a working electrode. The technical routine is shown as Scheme 1.

2.4. Cyclic voltammogram measurement

All measurements were carried out with a three-electrode system using a saturated $\text{Ag}|\text{AgCl}$ reference electrode as a reference electrode, a nickel electrode as a working electrode, and a platinum electrode as a counter electrode.

2.5. Modification of the nickel electrode

Modification was applied with a three-electrode system. A saturated $\text{Ag}|\text{AgCl}$ reference electrode was used as a reference electrode, a nickel electrode was used as a working electrode, and a platinum electrode was used as a counter electrode. Constant potential electrodeposition was undertaken at -0.35 V in the solution of $0.1 \text{ M Na}_2\text{HPO}_4$ at pH 7 for about 5 h. After that, the modified nickel electrode was dried by air to be tested.

2.6. Evaluation of the response characteristics of Ni-PME

All measurements were carried out with a two-electrode system using a saturated $\text{Ag}|\text{AgCl}$ electrode as a reference electrode and a nickel electrode as a working electrode.

2.7. SEM and EDS

Nickel plates ($0.1 \text{ mm} \times 50 \text{ mm} \times 50 \text{ mm}$) were carried out as a working electrode and the other conditions were the same to nickel rod electrode modification. Nickel plate and Ni-PME plate were measured by



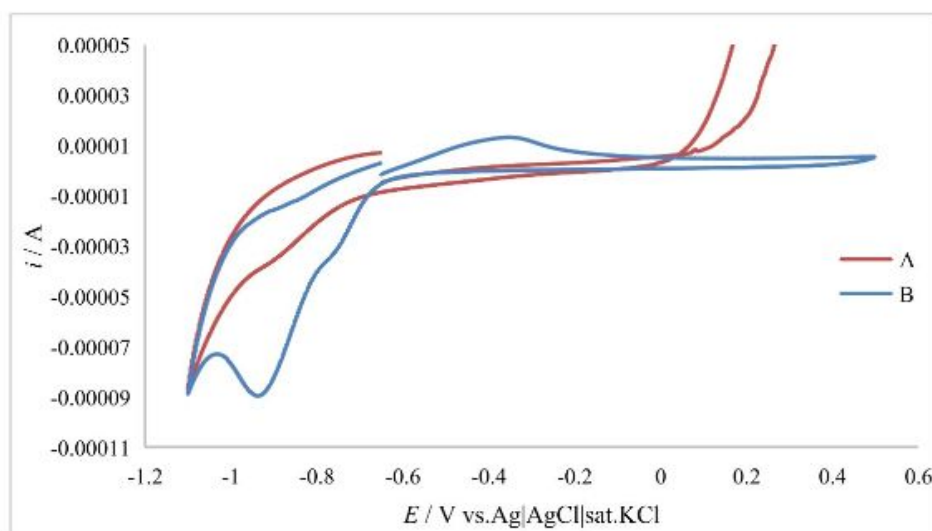


Figure 1. Cyclic voltammetry curves of Ni electrode in 0.1 M NaCl (A) and 0.1 M NaH_2PO_4 (B) at pH 7.

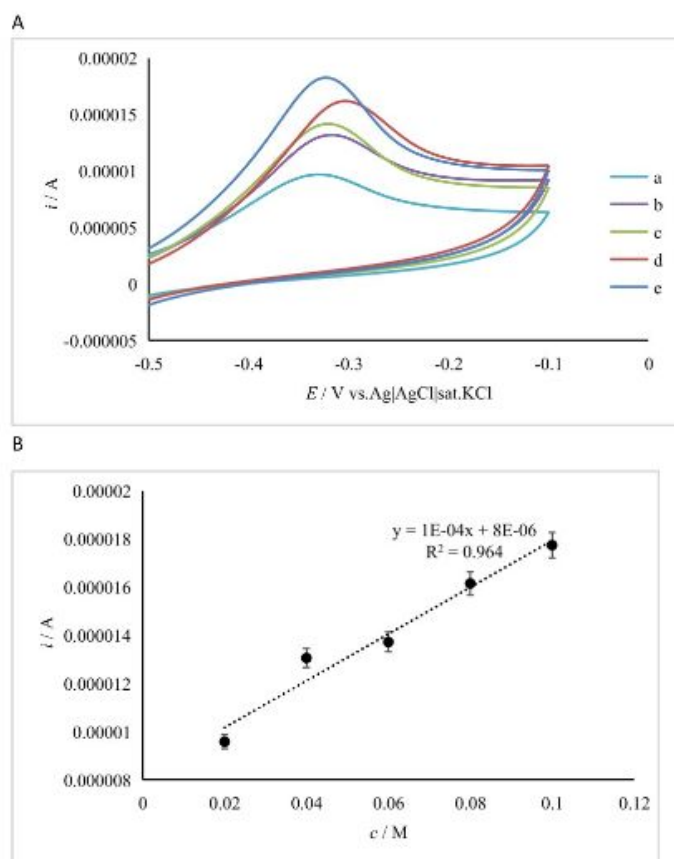


Figure 2. Cyclic voltammetry curves of Ni electrode in different concentrations of NaH_2PO_4 at pH 7 (A, a: 0.02 M; b: 0.04 M; c: 0.06 M; d: 0.08 M; e: 0.1 M.) and the relationship of concentration and peak current (B).

SEM and EDS.

3. Results and discussion

3.1. Electrochemical characteristics of nickel in NaH_2PO_4 solution

Firstly, the electrochemical properties of nickel electrode in the system with phosphate ion and without phosphate ion were compared

by cyclic voltammetry. The purpose of this experiment is to verify whether the metal nickel can have a specific electrochemical reaction with phosphate ions in the system containing phosphoric acid, so as to form an insoluble phosphate solid film. The scanning order was $-0.7 \text{ V} \rightarrow 0.5 \text{ V} \rightarrow -1.1 \text{ V} \rightarrow -0.7 \text{ V}$, and the scanning speed was 0.05 V s^{-1} . In Fig. 1A, there is no obvious electrochemical reaction of nickel electrode in 0.1 M sodium chloride solution at pH 7. Only anodic wave and cathodic wave can be observed from the cyclic voltammetry curve. Anodic signal is due to the oxidation of Ni. It can be said that nickel does not occur electrochemical reaction in the system without phosphate ion. As for Fig. 1B, in the sodium dihydrogen phosphate solution with pH 7 and concentration of 0.1 M, there is an obvious anodic peak at about -0.35 V and an obvious cathodic peak at -0.95 V . There are two cathode waves. By comparing the system with phosphate ion and the system without phosphate ion, it can be found that the cathode wave appears at about -0.95 V in both systems, and a cathode wave appears at about -0.8 V in the system with phosphate ion. Therefore, it can be judged that the cathode wave is generated by phosphate ion. Combined with the analysis in Fig. 1 (a), it can be inferred that these peaks may be the electrochemical reaction between nickel electrode and phosphate ion.

In order to further prove the above inference accurately and rigorously, we tested it by concentration dependent cyclic voltammetry. The electrochemical characteristics of nickel electrode at different concentrations of sodium dihydrogen phosphate were analyzed under the condition that the scanning sequence and scanning speed were consistent with the above tests. As shown in Fig. 2A, as the concentration of sodium dihydrogen phosphate solution increases, the anodic peak also increases. After analyzing the relationship between concentration and peak current (Fig. 2B), it is found that the relationship between concentration and peak current is approximately linear. This proves that the reaction at -0.35 V is indeed the reaction between nickel electrode and phosphate ion. The change of peak potential is considered to be caused by poor reversibility and repeatability of the reaction. There are two reasons. First, there is no obvious trend in the change of peak potential, especially in the concentration dependent cyclic voltammetry test, the peak potential swings left and right rather than moving in one direction. Second, when doing cyclic voltammetry test, we set the starting potential to -0.7 V in order to make the current as close as possible to 0 and reduce the degree of electrochemical reaction before the test as much as possible. But in fact, there will be a certain degree of electrochemical reaction each time. This will affect the position of peak potential to a certain extent, which brings uncertainty to the experimental results.

As well known, phosphoric acid is a ternary acid, which has three-



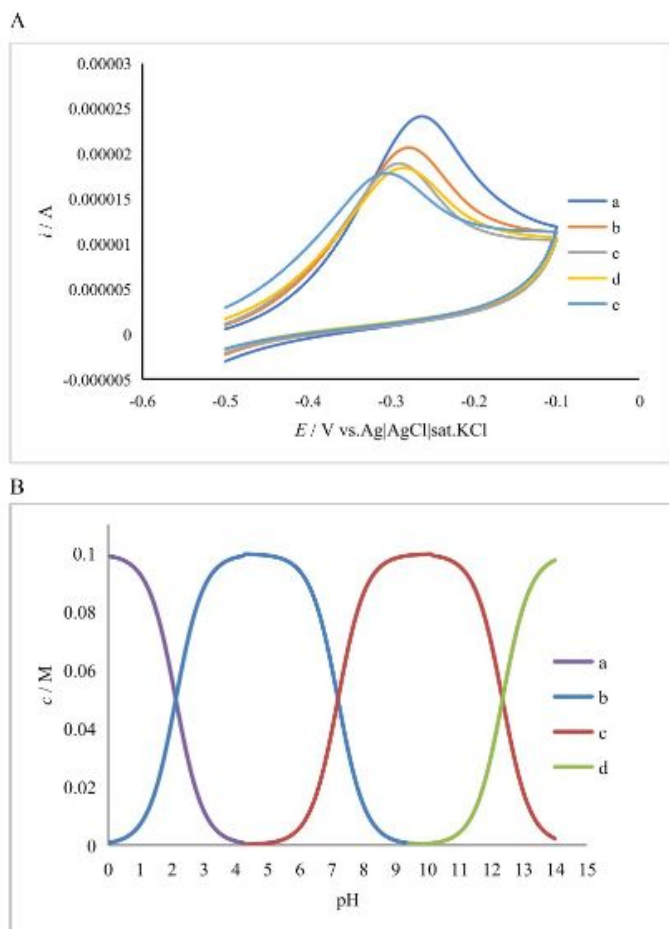


Figure 3. Cyclic voltammograms of Ni electrode in 0.1 M NaH₂PO₄ at different pH (A, a: pH 6.2; b: pH 6.4; c: pH 6.6; d: pH 6.8; e: pH 7.0) and phosphate ion species distribution of 0.1 M NaH₂PO₄ at different pH (B, a: H₃PO₄; b: H₂PO₄⁻; c: HPO₄²⁻; d: PO₄³⁻).

stage dissociation in aqueous solution, and the existing forms and distribution proportions of various valence phosphate ions are also different under different pH conditions. Under the condition of pH 7, monohydrogen phosphate ion and dihydrogen phosphate ion exist at the same time, and their relative distribution ratio is roughly similar. Therefore, in order to identify whether monohydrogen phosphate ion or dihydrogen phosphate ion reacts with nickel electrode in the above test, we conducted pH dependent cyclic voltammetry test. As shown in Fig. 3A, under the condition that the scanning sequence and scanning speed are consistent with the above test, the electrochemical characteristics of nickel electrode at different pH of sodium dihydrogen phosphate are analyzed. The anodic peak decreased with the increase of pH of sodium dihydrogen phosphate solution. The morphological distribution diagram of phosphate ion (Fig. 3B) is drawn through the calculation of Equation 1,2,3,4,5,6.



$$K_{a1} = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} = 7.5 \times 10^{-3} \quad (4)$$

$$K_{a2} = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]} = 6.23 \times 10^{-8} \quad (5)$$

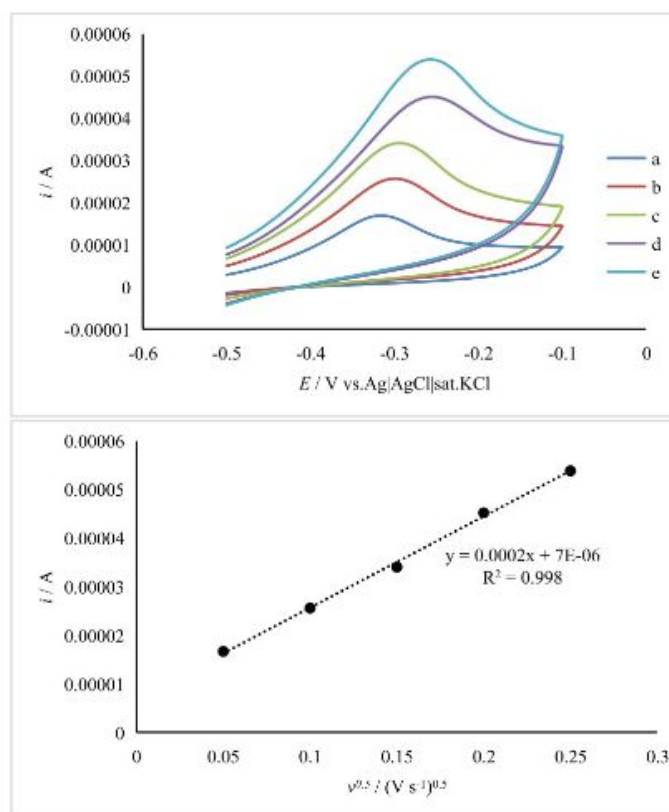


Figure 4. Cyclic voltammograms of Ni electrode in 0.1 M NaH₂PO₄ at pH 7 at different scan rate (A, a: 50 mV s⁻¹, b: 100 mV s⁻¹, c: 150 mV s⁻¹, d: 200 mV s⁻¹, e: 250 mV s⁻¹) and the relationship of scan rate and peak current (B).

$$K_{a3} = \frac{[\text{PO}_4^{3-}][\text{H}_3\text{O}^+]}{[\text{HPO}_4^{2-}]} = 2.2 \times 10^{-13} \quad (6)$$

Combined with the analysis of the two diagrams, it can be verified that dihydrogen phosphate ion reacts with nickel electrode.

In addition, we also studied the kinetic characteristics of the electrochemical reaction between nickel electrode and phosphate ion. Cyclic voltammetry at different scanning speeds was carried out in sodium dihydrogen phosphate solution with pH 7 and concentration of 0.1 M. As shown in Fig. 4A, the anodic peak also shows an upward trend with the increase of scanning speed. After analyzing the relationship between peak current and scanning speed, it is found that the arithmetic square root of peak current and scanning speed shows a good linear relationship (Fig. 4B). It can be said that the electrochemical reaction between nickel electrode and phosphate ion belongs to diffusion control reaction.

We also combined the potential pH diagram of nickel at 25 °C [22]. It can be seen from Fig. S1 that under the condition of pH 7, the dissociation reaction of nickel occurs at about -0.3 V, that is, from solid nickel (Ni_{Cr}) to ionic nickel ion (Ni²⁺). Through the previous cyclic voltammetry curve, we have also proved that the phosphate ion electrochemically reacting with the nickel electrode is dihydrogen phosphate ion rather than monohydrogen phosphate ion. Therefore, we can judge that the following reactions have taken place on the electrode surface.



However, nickel has a variety of oxide forms with different valence states, so the mixed potential response occurs on the electrode surface, so the response slope deviated the Nernstian response slope.



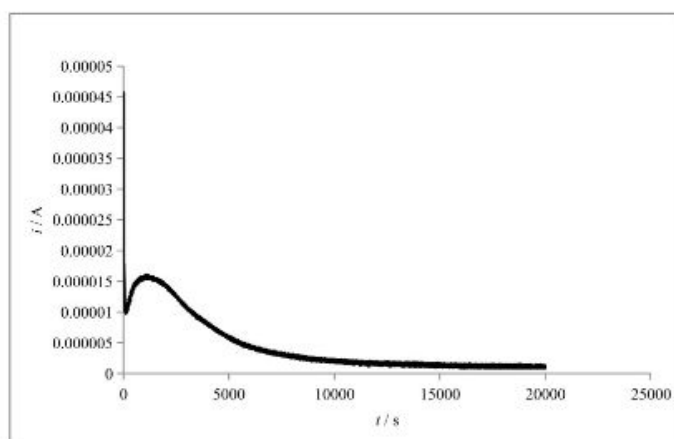


Figure 5. Current-time curve of Ni electrode in 0.1 M NaH_2PO_4 solution at the constant potential of -0.35 V

3.2. Modification of the nickel electrode

In the previous cyclic voltammetry experiments, we have explored the best modification conditions of nickel electrode. Therefore, the nickel electrode was electrochemically modified under the previously determined conditions. In the sodium dihydrogen phosphate solution with pH 7 and concentration of 0.1 M, the nickel electrode was used as the working electrode, Ag|AgCl electrode as the reference electrode and platinum electrode as the counter electrode. The constant potential electrolysis method was adopted, and the constant potential was set to -0.35 V. As shown in Fig. 5, in the initial stage, the electrolytic current was about $10 \mu\text{A}$. Then the current began to rise because the nickel electrode dissociated from solid metal nickel to nickel ion. After corrosion, the surface area of the nickel electrode increased, resulting in the increasing of current. The current reached its maximum value after increasing for about 15 min, about $15 \mu\text{A}$. Then the current began to decrease gradually. This is because a layer of oxide film was formed on the surface of nickel electrode, which played the role of passivation, thus blocking the corrosion of nickel electrode. At the same time, nickel oxide

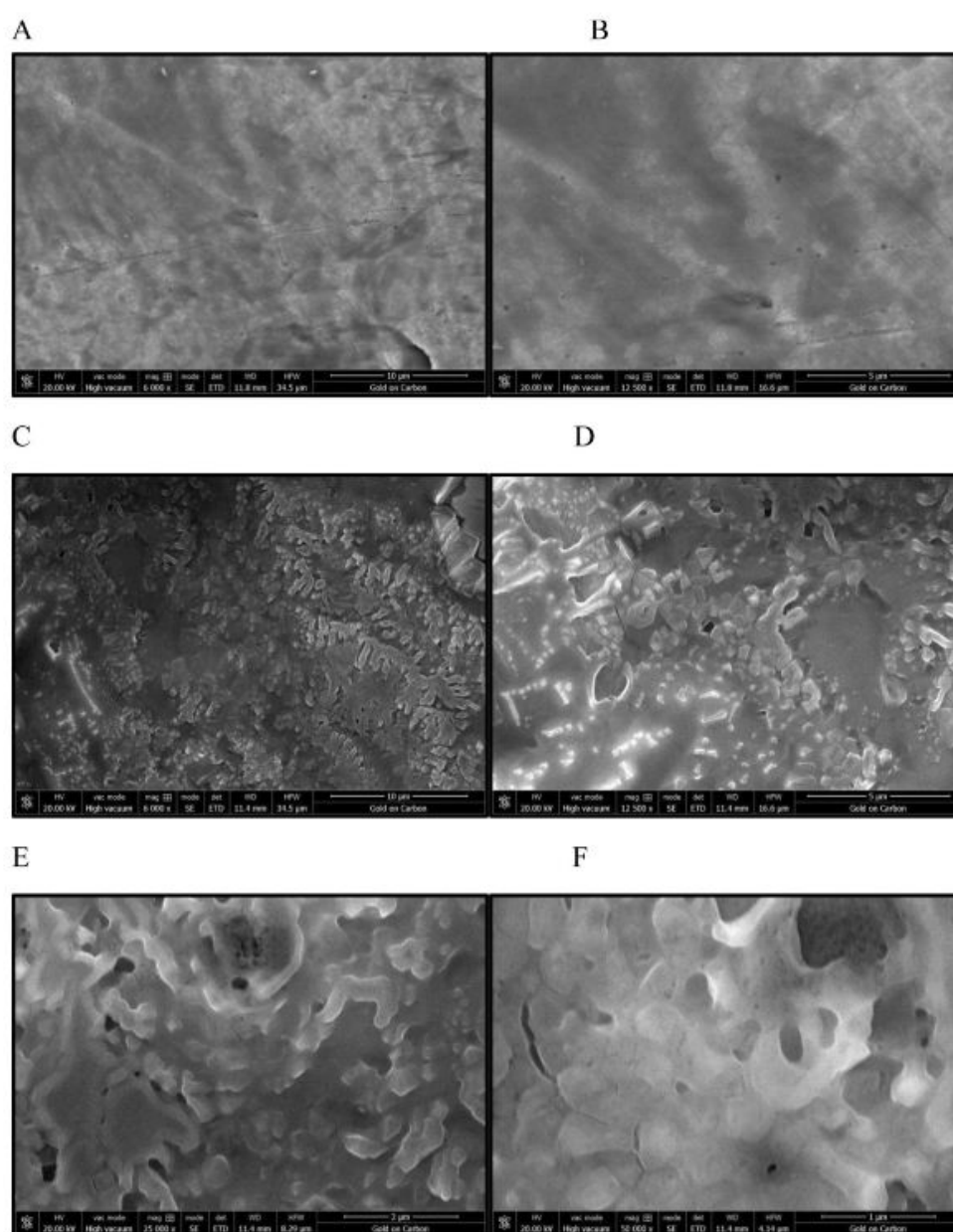


Figure 6. SEM images of the surface of Ni (A and B) and Ni-PME (C-F)



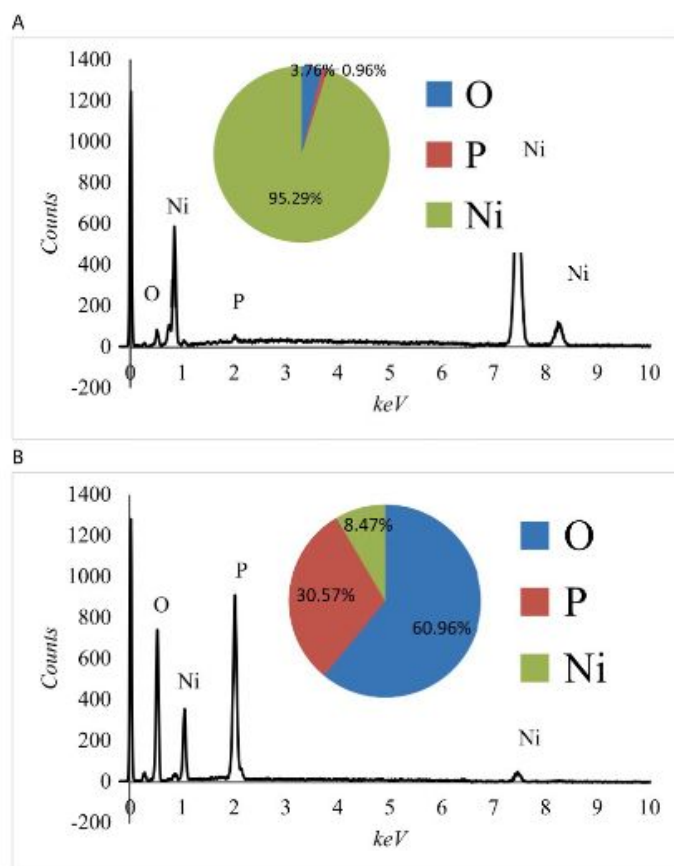


Figure 7. Energy dispersive spectrometry of Ni(A) and Ni-PME(B): Insert figure: Mass distribution of various elements.

also reacts with phosphate ions to form nickel phosphate compounds on the surface of nickel electrode. With the progress of electrodeposition, phosphate compounds on the surface of nickel electrode gradually accumulated and covered the surface of nickel electrode. Therefore, the current gradually decreases. After about 4 h, the current wirelessly approached 0 A and did not change. At this time, we finished the constant potential electrodeposition, took the nickel electrode out of the electrolyte and dried it naturally for material characterization and sensor performance evaluation.

3.3. SEM and EDS analysis of the Ni-PME

Firstly, we compared the unmodified pure metal nickel electrode with the modified Ni-PME by scanning electron microscopy (SEM). As shown in Fig. 6 (A and B), no obvious morphological features were observed on the surface of unmodified pure metal nickel electrode, whether 6000 times or 12500 times, and only some fine surface scratches were observed. In Ni-PME, coral like substances can be observed on the surface of Ni-PME at 6000 times (Fig. 6C). With the magnification of 12500 times, 25000 times and 50000 times (Fig. 6D, E and F), the crystal structure gradually growing on the electrode surface can be clearly observed. These compounds are phosphate compounds with different forms of nickel produced by electrochemical modification.

In order to explore the surface compound composition of electrochemically modified Ni-PME, the element composition and relative distribution ratio of the two electrode surfaces before and after modification were analyzed and compared by EDS method. In the unmodified pure metal nickel electrode (Fig. 7A), there are three obvious peaks, which are 1 keV, 7.5 keV and 8.2 keV respectively. These three peaks are the peaks of nickel element. Through the statistics of atomic mass ratio,

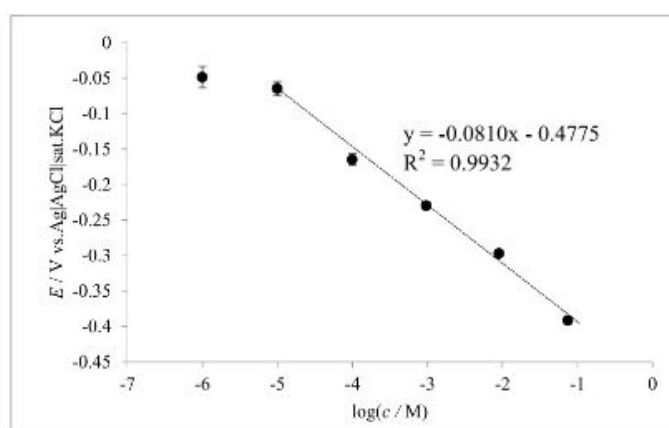


Figure 8. Response characteristics of Ni-PME in NaH_2PO_4 standard solution at pH 4.

it can be concluded that 95.28% of the surface of unmodified nickel metal electrode is nickel element, 3.76% is oxygen element and 0.96% is phosphorus element. The detection of oxygen may be attributed to the slow oxidation on the surface of nickel electrode, while phosphorus may be an impurity. On the electrode surface of electrochemically modified Ni-PME, the detection ratio of nickel, oxygen and phosphorus changed significantly (Fig. 7B). The relative proportion of oxygen-containing compounds reached 60.96%, and the relative proportion of phosphorus-containing compounds reached 30.57%. As for nickel containing compounds, the relative proportion decreased from 95.29% to 8.47%. These conclusions also further verify the above conclusions, that is, nickel oxides and nickel phosphate compounds formed on the electrode surface after electrochemical modification. In this way, the phosphate ion response mechanism of Ni-PME is explained clearly. We can determine that nickel oxides are involved in the mixed potential response, but there are many kinds of nickel oxides, so we can't simply judge them by EDS, so Ni_mO_n is used instead. In addition, through the previous CV, we have proved that the phosphate ion participating in the reaction is H_2PO_4^- . Therefore, based on the above analysis, the Equation 9 is obtained.



3.4. Response characteristics of the Ni-PME

3.4.1. Response slope and detection linear range

As shown in Fig. 8, in sodium dihydrogen phosphate solution at pH 4, Ni-PME can respond to phosphate ion concentration from 10^{-5}M to 0.1M , with a response slope of -81.0 mV dec^{-1} and R^2 of 0.9937. The reason why the response slope exceeds the theoretical slope of Nernst response (-59.1 mV dec^{-1}) is that the potential response is a mixed potential response due to the different types of nickel oxides and phosphate compounds. In addition, we tested phosphate standard solutions at different pH (Fig. S2). It was found that with the increasing of pH, the response slope of Ni-PME decreased and the linear range decreased. This is due to the change in the relative content of H_2PO_4^- ions. In the previous Fig. 3B, we have discussed that the relative content of H_2PO_4^- ions will decrease with the increase of pH in the range of pH 4-7, while Ni-PME can only specifically respond to H_2PO_4^- ions. Therefore, when the pH exceeds 7, the response of Ni-PME to phosphate ions gradually disappears. In the actual detection, the concentration of phosphate ion in the sample should be accurately calculated with the use of pH meter.

3.4.2. Selectivity

The selectivity of Ni-PME was evaluated by the mixed solution method [3], and the calculation method is shown in Equation 10.



Table 1
Selectivity coefficient of common anions measured by mixed solution method

Anion	$\log K_{pot}$
NO ₃	2.3±0.2
Cl	4.8±0.2
SO ₄ ²⁻	4.2±0.3
HCO ₃	2.3±0.3
Ac	3.2±0.2

Table 2

Real sample test comparing to conventional phosphomolybdate blue spectrometer

Sample	Ni-PME (mM)	Colorimetry (mM)
Coca Cola	1.9 ± 0.2	2.1 ± 0.1
Orange juice	4.6 ± 0.2	4.8 ± 0.1
Waste water	2.3 ± 0.2	2.1 ± 0.2

$$E_{ISE} = E' + \frac{RT}{nF} \ln \left(a_B + K_{B,A}^{pot} a_A^{\frac{n_A}{n_B}} \right) \quad (10)$$

In the selectivity evaluation test, we selected five common inorganic and organic anions, namely nitrate ion, chloride ion, sulfate ion, bicarbonate ion and acetate ion. By calculating the selectivity coefficient, it is found that the selectivity coefficient of all common anions in Table 1 is below -2, which means that when the concentration of other interfering ions is less than 100 times that of the target ion phosphate ion, the interfering ions will not affect the electrode potential of Ni-PME.

3.4.3. Response time

In terms of response time, we use t_{95} [3] to evaluate Ni-PME. Ni-PME was put into 10⁻⁵ M sodium dihydrogen phosphate solution. After the potential was stable, put it into 10⁻⁴ M to 0.1 M solution to be tested quickly and continuously. As shown in Fig. S3, by calculating the response time, it is found that the t_{95} of Ni-PME is less than 20 s at all concentrations.

3.4.4. Stability

In order to evaluate the long-time real-time online monitoring ability of Ni-PME for phosphate ions, we put Ni-PME into 0.1 M NaH₂PO₄ solution for real-time monitoring for 24 hours. As shown in Fig. S4, the potential fluctuation is ±3 mV.

The fluctuation of potential is caused by the change of temperature.

3.4.5. Lifetime

In order to evaluate the lifetime of Ni-PME, we conducted a performance test once a week. As shown in Fig. S5, the potential of Ni-PME basically did not change in the first four weeks, and the response slope decreased after the fifth week. After the tenth week, the response slope not only decreased, but also the linear range decreased significantly, basically losing the response ability to phosphate ions. Therefore, it can be said that Ni-PME can be used continuously for more than 4 weeks, and it needs to be modified after more than 4 weeks.

3.4.6. Real sample test

In order to test the phosphate ion response ability of Ni-PME in actual liquid samples, we compared the test results of Ni-PME with the traditional molybdenum blue colorimetry. Dihydrogen phosphate ion is one of the existing forms of phosphate, and its respective proportion is determined by the pH of the solution. When pH is constant, the ratio of dihydrogen phosphate ion to total phosphate is fixed, and dihydrogen phosphate ion cannot exist in any system alone. The method we use is to directly detect the concentration of dihydrogen phosphate ion through ion selective electrode, and then indirectly calculate the concentration of total phosphate combined with pH value. In actual analysis and

Table 3

Recovery test in different solution

Sample	Added (mM)	Found (mM)	Recovery rate (%)
Distilled water	10.0	9.9 ± 0.1	99
Tap water	10.0	9.8 ± 0.1	98
Milk	10.0	9.6 ± 0.3	96

Table 4

Response characteristics comparison of references and current research

Sensing ion	Sensing element/structure	Detection range (M)	Slope (mV dec ⁻¹)	Ref.
HPO ₄ ²⁻	Nano-IIP/CP	10 ⁻⁵ –10 ⁻¹	30.6	[23]
HPO ₄ ²⁻	PTFE-Ag ₃ PO ₄ ·Ag ₂ S	10 ⁻⁵ –10 ⁻¹	32.6	[24]
HPO ₄ ²⁻	CuMAPc-PnBA coated Au electrode	4 × 10 ⁻⁹ –10 ⁻²	29.8	[25]
HPO ₄ ²⁻	Mo electrode	10 ⁻⁵ –10 ⁻¹	26.9	[26]
H ₂ PO ₄ ⁻	Co modified electrode	10 ⁻⁵ –10 ⁻¹	55.2	[27]
H ₂ PO ₄ ⁻	Nickel modified electrode	10 ⁻⁵ –10 ⁻¹	81.0	Current research

testing, total phosphate is often detected. We selected Coca Cola, orange juice and laboratory wastewater as test samples. Each sample was tested three times. Ionic strength of the actual sample was tested and then prepared the corresponding standard solution for test. As shown in Table 2, the phosphate ion concentration of the sample tested by Ni-PME is very close to that of molybdenum blue colorimetry, which also proves that Ni-PME has the ability to detect actual liquid samples.

3.4.7. Add recovery test

Subsequently, we conducted the addition recovery test. The samples to be tested were distilled water, tap water and milk. Sodium dihydrogen phosphate solution was added to each sample to make its concentration reach 10 mM. Each sample was tested three times. As shown in Table 3, Table 4, in all samples, the recovery of Ni-PME is more than 96%.

4. Conclusion

In this study, a phosphate ion sensor was designed and developed by electrochemical modification based on nickel metal electrode. Firstly, the potential (-0.35 V) required for constant potential electrolysis was determined by cyclic voltammetry. Subsequently, the nickel electrode was specifically modified to produce a response to phosphate ions in the solution. The surface morphology and elemental composition of Ni-PME were characterized and analyzed by SEM and EDS, and the mechanism of its response to phosphate ion was explained. The phosphate ion response of Ni-PME was evaluated in a two electrode system. The results show that under the condition of pH 4, Ni-PME can respond to phosphate ions with a concentration of 10⁻⁵ M to 0.1 M, the response slope is -81.0 mV dec⁻¹, and the selectivity coefficients for common anions are below -2. The response time is less than 20 s. The stability of electrode potential is very high, and the fluctuation of 24-hour continuous test potential is within ±3 mV. The service life is more than 4 weeks. Compared with the traditional blue molybdenum colorimetry, Ni-PME showed good effect and good addition recovery.

CRediT authorship contribution statement

Kebin Xu: Conceptualization, Formal analysis, Funding acquisition, Investigation, Methodology, Resources, Software, Supervision, Validation, Writing – original draft. **Binyu Wu:** Investigation, Data curation, Formal analysis, Visualization, Validation. **Junliang Wan:** Investigation, Data curation, Formal analysis, Visualization, Validation. **Ying Li:** Funding acquisition, Project administration, Supervision, Writing – review & editing. **Min Li:** Funding acquisition, Writing – review & editing.



Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper

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Supplementary materials

Supplementary material associated with this article can be found, in the online version, at [doi:10.1016/j.electacta.2022.140065](https://doi.org/10.1016/j.electacta.2022.140065).

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