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Phosphate Ion-Selective Electrode Based on Electrochemically Modified Iron

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iron electrode to enable reaction with phosphate ions. Scanning electron microscopy and energy dispersive X-ray spectroscopy were used to characterize and analyze the morphology and elemental composition of Fe-PME, elucidating how it responds to phosphate ionation. The two-electrode system was then utilized for the evaluation of the phosphate ion response of Fe-PME at pH 4. Fe-PME's response to phosphate ions is demonstrated by the results, ranging from 10^{-5} to 0.1 M and with a slope of -52.8 mV dec⁻¹. Fe-PME exhibited satisfactory results when compared to the conventional blue colorimetry of molybdenum.

1. INTRODUCTION

Phosphorus is a crucial component of DNA and RNA in cells, contributing significantly to biological processes such as growth, development, and genetic metabolism. Most of the soluble phosphates in natural water are composed of various valence orthophosphates, mainly in the form of $H_3PO_4^{-1}$ which can be absorbed by algae as nutrients. Other forms of soluble phosphates, including organophosphates contained in pesticides, will also be gradually decomposed into orthophosphates.^{2,3} These include organophosphates contained in pesticides and fertilizers and polyphosphates contained in the washing powder.

iron oxide and its phosphate were modified onto the surface of the

Lately, due to the ongoing progress of industry and agriculture, there has been a concerning increase in wastewater discharge, causing an imbalance in the ecological environment. The high levels of phosphorus cause water eutrophication and the rapid growth of toxic algae, leading to a decrease in dissolved oxygen levels, deterioration of water quality, and the death of aquatic organisms. It is standard practice in clinical diagnosis to test for serum phosphate levels. Valuable reference information for diagnosing hyperparathyroidism, vitamin D deficiency, and other diseases can be found in the phosphate level of body fluid.⁴Attention to phosphate determination is a matter of great importance not only from the ecological

environment but also from biomedicine. Despite numerous accounts on the methods for determining phosphate, technical issues remain in achieving precise, swift, and instantaneous monitoring of phosphate. Murphy and Riley's molybdenum blue colorimetry is currently the accepted technique for detecting phosphate in aqueous solution, as evidenced by published articles that have primarily employed colorimetry, chromatography, fluorescence spectroscopy, and electrochemical methods.^{5–8}As part of this process, ascorbic acid is utilized as a reducing agent along with the addition of ammonium molybdate, ascorbic acid, and antimony(III) to phosphate samples in order to create a blue phosphomolybdate complex, which is then analyzed for phosphate concentration using a spectrophotometer. The experimental process is cumbersome and lengthy; the operating environment requires high requirements; online monitoring cannot be realized; and the chemicals used in the operation are harmful to health. The

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Figure 1. Schematic diagrams for illustrating the preparation, fabrication, modification, and characterizations of Fe-PME as a basis of potentiometric phosphate ion sensors.

electrochemical sensor method has the advantage of making up for some of the above defects. The advantages of this system are its straightforward functioning, ease of transport, high sensitivity, minimal detection boundary, and the ability to analyze analytes in a continuous and expeditious manner.^{9,10} The difficulty of its detection technology lies in the fact that phosphoric acid is a strong ternary acid and phosphate saline solution has tertiary dissociation. This means that the distribution form and proportion of phosphate are different under different pH conditions, which brings difficulties to quantitative analysis and real-time monitoring of phosphate. The ability of ion-selective electrodes to recognize only a certain ion with good recognition is the reason why phosphate solutions usually comprise phosphate, monohydrogen, and dihydrogen ions. As the pH changes, the distribution ratio of these three ions also changes, making the quantitative detection of phosphates unpredictable. So we can only detect it meaningful at the same time as the pH of the solution to be tested. Chitosan smectite biological composite was utilized by Topcu et al.¹¹ as an electroactive element in the PVC membrane potential sensor design, enabling precise and specific detection of HPO₄²⁻ ions. The potentiometric ionselective electrode (PISE) is used at the concentration of 1 \times $10^{-6}-1 \times 10^{-2}$ M. HPO₄²⁻ aqueous solution showed good potential response, and the detection limit was 6×10^{-7} M. In addition, organotin ionophores are also integrated into PVC films. Tin(IV) promotes the combination of oxygen atoms in phosphate and organic complexes by taking electrons out of the center. Liu et al.¹² doped binuclear organotin compounds into liquid polymer films as phosphate ionophores. In the range of $5 \times 10^{-6} - 10^{-1}$ M, its detection limit is a satisfactory 10^{-6} M, which meets environmental water sample monitoring requirements; however, service performance drops drastically after one month. Additionally, there are reports on solid-state selective detection based upon other materials and theories,^{13,14} such as screen-printed electrode (SPE), molecular imprinted sensor (MIP), field effect transistor, etc., that demonstrate excellent results. Kabir et al. introduced a novel screen-printed electrode enhanced with silver nanowires covered in ammonium molybdate tetrahydrate (AMT/ agnms). This electrode demonstrates exceptional sensitivity toward phosphate within the range of $5 \times 10^{-6} - 1 \times 10^{-3}$ M, with a detection limit of 3×10^{-6} M, surpassing the performance of other metal-modified electrodes. Xiao et al.

proposed an all-solid-state phosphate ion sensor modified with cobalt phosphate on the surface of metal cobalt electrode, revealing its response mechanism to three different valence phosphates at different pHs.¹⁵ Meruva et al. based on the research of Dan et al. elucidated that the potential response of a modified cobalt electrode to phosphate ion is a mixed potential response mechanism, utilizing CV and XPS.¹⁶ Xu et al. used electrode surface modification technology to modify cobalt,¹⁷ molybdenum,¹⁸ and tungsten;¹⁹ the electrochemical response mechanism of phosphate ion sensor was further analyzed; and the actual detection standard curves based on different pH were established. We also studied modifying nickel electrodes to detect phosphate ions in the early stage. Although the response performance is excellent, nickel is a toxic heavy metal and cannot meet the practical needs of realtime in vivo online monitoring.

Exploring the mechanism, this study's research object of iron is chosen to begin by seeking a metal material with properties akin to cobalt. Comparing it to cobalt will uncover any similarities in its reaction characteristics and further expose the mixed potential's reaction mechanism. It is also used as evidence to explain the cobalt response mechanism.

While other studies may have explored cobalt-, molybdenum-, and tungsten-based electrodes, the Fe-PME introduces iron as a less toxic and more economically viable alternative. Its cost and toxicity make it more desirable for wide use, particularly in the fields of environmental surveillance and food analysis, where cost-efficiency and security are essential. On the basis of the above research, this study makes use of the similar chemical properties of Fe and Co to deeply analyze the electrochemical properties of Fe in phosphate ion solution and then specifically modify Fe to make it responsive to phosphate ion as a Fe-PME (Fe-phosphate-modified electrode). A new electrochemical sensor for phosphate ions was created. The design pathway is illustrated in Figure 1.

2. EXPERIMENTAL SECTION

2.1. Materials and Reagents. All of the chemicals utilized in the trial were classified as analytical grade and were employed without undergoing further refinement. Solutions were prepared utilizing ultrapure water with a resistivity measuring 18.2 M Ω cm. We purchased the following chemicals from Xinke in Shenyang, China: disodium hydrogen phosphate (Na₂HPO₄), sodium bicarbonate (NaHCO₃), sodium acetate



Figure 2. (A) Cyclic voltammetry curves of Fe electrode in 0.1 M NaCl (a) and 0.1 M NaH₂PO₄ (b) at pH 7; (B) Cyclic voltammetry curves of Fe electrode in different concentrations of NaH₂PO₄ 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 at -0.57 V (C), -0.45 V (D), and -0.03 V (E); (F) Cyclic voltammetry curves of Fe electrode in 0.1 M NaH₂PO₄ at different pHs (a: pH 5.8; b: pH 6.0; c: pH 6.2; d: pH 6.4; e: pH 6.6; f: 6.8); (G) Relationship of concentration of phosphate ion and peak potential; (H) Phosphate ion species distribution of 0.1 M NaH₂PO₄ at different pHs (a: H₃PO4; b: H₂PO₄⁻⁷; c HPO₄²⁻⁷; d: PO₄³⁻) and the relationship between practical concentration of H₂PO₄⁻⁷ in 0.1 M NaH₂PO₄; (I) Relationship of practical concentration of H₂PO₄⁻⁷ and peak current at -0.57 V.

(NaCH₂COOH), sodium chloride (NaCl), sodium sulfate (Na₂SO₄), hydrochloric acid (HCl), and sodium hydroxide (NaOH). Additionally, we acquired iron rods (diameter 2 mm, length 100 mm, purity 99.99%) and iron plates (thickness 0.1 mm, dimensions 50 mm \times 50 mm) from Guantai Metal in Tianjin, China.

2.2. Apparatus. A Quanta250-FEG scanning electron microscope manufactured by FEI in the Czech Republic was utilized for SEM analysis, in combination with energy-dispersive spectrometry. EDS analysis was carried out using an X-MAX-20 instrument made by Oxford Instruments in the United Kingdom A Versastat3 electrochemical workstation (Ametek, USA) was employed to conduct electrochemical measurements.

2.3. Preparation of the Iron Electrode. After a 1 min polish of the iron wire (φ 2 mm × 100 mm) with sandpapers of #80, #240, and #1000, it was washed for 30 min with an ultrasonic cleaner. One end of the iron wire was covered with a polytetrafluoroethylene (PTFE, φ 10 mm × 20 mm) tube as a working electrode. Figure 1 displays the technical routine.

2.4. Cyclic Voltammogram Measurement. Each measurement was conducted utilizing a three-electrode setup, with a saturated AglAgCl reference electrode serving as the reference, an iron electrode as the working electrode, and a platinum electrode as the counter electrode.

2.5. Modification of the Iron Electrode. An adjustment was made by using a three-electrode setup consisting of a saturated AglAgCl reference electrode, an iron working electrode, and a platinum counter electrode. A constant potential deposition process was carried out at -0.57 V in a solution of 0.1 M Na₂HPO₄ with a pH of 6 for approximately 5 h. Subsequently, the iron electrode that had been modified was air-dried before being tested.

2.6. Evaluation of the Response Characteristics of Fe-PME. The measurements were conducted by using a twoelectrode system, with a saturated AglAgCl electrode serving as the reference electrode and an iron electrode serving as the working electrode. We compared the actual sample testing and addition recovery testing with the molybdenum blue colorimetric method.⁵ We used a mixed solution method for the selectivity experiment, which fixes the concentration of phosphate ions, gradually increases the concentration of corresponding interfering ions, and then calculates the selectivity coefficient.¹⁷

2.7. SEM and EDS. An iron plate (dimensions: $0.1 \text{ mm} \times 50 \text{ mm} \times 50 \text{ mm}$) was used as the working electrode, while all other conditions were kept consistent with the modification of the iron rod electrode. Iron plate and Fe-PME plate were measured by SEM and EDS.



Figure 3. (A) Current–time curve of Fe electrode in 0.1 M NaH₂PO₄ solution at pH 6 at the constant potential of -0.57 V; SEM images of the surface of Fe (B) and Fe-PME (C); Energy-dispersive spectrometry of Fe (D) and Fe-PME (E).

3. RESULTS AND DISCUSSION

3.1. Electrochemical Characteristics of Iron in NaH₂PO₄ **Solution.** To investigate the electrochemical properties of an iron electrode in a phosphate-ion-containing system, we initially tested the cyclic voltammetry curve of a pure metal iron electrode in a sodium chloride solution at pH 7. The scanning sequence is $-0.7 \rightarrow -0.2 \rightarrow -0.9 \rightarrow -0.7$ V. As shown in Figure 2A (a), except for the reaction of Fe \rightarrow Fe²⁺, no other obvious redox peaks were observed, which indicates that iron basically does not undergo redox reaction in the system without phosphate ion. Then, we measured the cyclic voltammetry curve of the pure metal iron electrode in sodium dihydrogen phosphate solution at pH 7. The scanning sequence was $-0.7 \rightarrow 0.3 \rightarrow -0.9 \rightarrow -0.7$ V. The results show that there are three anodic peaks at -0.57, -0.45, and -0.03 V, respectively, which indicates that a series of electrochemical reactions have taken place at the iron electrode in the system containing phosphate ions.

We conducted a concentration-dependent cyclic voltammetry analysis to delve deeper into the characteristics of these electrochemical reactions. As depicted in Figure 2B, the response of the three anodic peaks to the concentration of phosphate ion in the solution is different. By comparing Figure 2C, the correlation between the anodic peak at -0.57 V and phosphate ion concentration is highly linear, with an *R* square of 0.995; likewise, the two anodic peaks at -0.45 V have a positive relationship to phosphate ion concentration (R square of 0.896), likely due to their close proximity. Figure 2E reveals no clear linear correlation between the anodic peak current and phosphate ion concentration, which is 0.03 V in magnitude. Therefore, through the above tests, we can preliminarily analyze that the anodic peak at -0.57 V is the direct electrochemical reaction between iron and phosphate ions, while the other two peaks may be some indirect electrochemical reactions.

Preliminary tests demonstrate that the peak at -0.57 V is a direct electrochemical reaction between iron and the phosphate ion; however, due to phosphoric acid being a ternary acid, tertiary dissociation occurs in aqueous solutions, and the form and amount of phosphate ions vary depending on pH conditions. Therefore, in order to analyze which phosphate ion reacts with the iron electrode, we conducted a pHdependent cyclic voltammetry test to test the electrochemical properties of the iron electrode in sodium dihydrogen phosphate solution with a certain concentration but different pHs. As shown in Figure 2F, as the pH rises, the anodic peak at -0.57 V shifts toward a more positive potential direction, leading to a gradual decrease in peak current. A similar trend is observed with the anodic peak at -0.45 V due to its proximity. As for the anodic peak of -0.03 V, there is no obvious change pattern through the cyclic voltammetry curve, which is also consistent with the results of the previous concentration dependence test. It can be seen from Figure 2G that at a pH range of 6.0–6.8, the peak potential shifts from -0.57 to -0.49V as the pH and peak potential exhibit a strong linear relationship (R squared value of 0.999). Figure 2H displays the distribution curve of different phosphate ion forms, computed based on all dissociation constant levels of phosphoric acid using the provided equations:

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$$
(1)

$$H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$$
 (2)

$$HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$$
 (3)

$$K_{a1} = \frac{[H_2PO_4^{-}][H_3O^{+}]}{[H_3PO_4]} = 7.5 \times 10^{-3}$$
(4)

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

$$K_{a3} = \frac{[PO_4^{3^-}][H_3O^+]}{[HPO_4^{2^-}]} = 2.2 \times 10^{-13}$$
(6)

According to this curve, we calculated the practical relative content of dihydrogen phosphate ion at different pH values and explored the relationship between it and peak current. As shown in Figure 2I, the concentration of dihydrogen phosphate ion shows a linear negative correlation with the peak current, which shows that the phosphate ion undergoing electrochemical reaction at the iron electrode is dihydrogen phosphate ion.

3.2. Surface Modification and Characterization of Iron Electrode. 3.2.1. Surface Modification. Through a series of cyclic voltammetry tests, we have determined that the anodic peak at -0.57 V is the electrochemical reaction of iron with a dihydrogen phosphate ion. Therefore, we used constant potential electrolysis to specifically modify the surface of the

iron electrode to produce iron phosphate compounds on the surface, so as to produce sensitive substances with specific response to phosphate ion. As shown in Figure 3A, the starting current is about 6 μ A. For a period of time, it began to increase to about 10 μ A, which was caused by the increase of surface area caused by corrosion on the iron surface, then the current gradually decreased, and finally infinitely close to 0 A. Prior to corrosion, the working electrode was a pristine iron one. As corrosion took place, iron oxides and phosphate compounds gradually adhered to the iron electrode's surface, thus reducing its effective reaction area and consequently diminishing peak current. After electrolysis, the electrode was placed in air for natural air drying to prepare for surface characterization and a phosphate ion response test.

3.2.2. SEM and EDS Analysis. The morphological characteristics of the pure metal iron electrode surface and Fe-PME surface were observed and compared by scanning electron microscope. As shown in Figure 3B, the surface of pure metal iron electrode is smooth and neat without obvious morphological characteristics. In Figure 3C, it can be clearly observed that massive crystals are formed on the surface of Fe-PME, with a thickness of about 1 μ m. This may be the crystal structure of the iron phosphate compounds.

In order to further verify this hypothesis, EDS analysis of the iron electrode and Fe-PME surface was carried out. It can be seen from Figure 3D that there are only iron peaks and a small amount of unknown impurity peaks (5.2 keV) on the surface of pure metal iron electrode. In Fe-PME samples, Figure 3E, the relative contents of oxygen and phosphorus increased significantly, accounting for most of the atomic weight. This also supports our previous conclusions in the cyclic voltammetry test. Combined with the analysis of potential pH diagram of iron (Figure S1), the response mechanism of Fe-PME is shown in the following formula

$$\operatorname{Fe}^{2+} + 2e^{-} \rightleftharpoons \operatorname{Fe}$$
 (7)

$$Fe + 2H_2PO_4^- \rightleftharpoons Fe(H_2PO_4)_2 + 2e^-$$
(8)

$$4Fe + 3O_2 + 3H_2O \rightleftharpoons 2Fe_2O_3 \cdot 3H_2O \tag{9}$$

$$3Fe_2O_3 + 4H_2PO_4^- + 10H^+ + 6e^-$$

$$\approx 2Fe_3(PO_4)_2 + 9H_2O \qquad (10)$$
The peak of -0.45 V has been fully demonstrated through

The peak of -0.45 V has been fully demonstrated through concentration-dependent experiments (Figure 2B) as a reaction between iron and phosphate ions; the peak of 0.03 V is inferred to be an oxidation reaction of iron based on the potential pH diagram of iron (Figure S1). Iron undergoes an indirect electrochemical reaction where it is initially oxidized to iron oxide, which then combines with phosphate ions to produce iron phosphate compounds; during this process, oxides play a crucial role as an intermediate product.

3.3. Performance Test of Fe-PME. After analyzing the phosphate ion response mechanism of Fe-PME, we evaluated the phosphate ion response ability of Fe-PME using the twoelectrode system, namely, the resting potential method. As shown in Figure 4, the results indicate that Fe-PME's response to phosphate ion falls within a linear range from 10^{-5} to 10^{-1} M, with a response slope of -52.8 mV dec⁻¹. The discrepancy in the response slope from the theoretical value of -59.1 mV dec⁻¹ is attributed to the mixed potential of the response electrode. We also evaluated the response characteristics of Fe-PME in standard solutions with different pHs. As shown in



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

Figure S1, the response slope of Fe-PME to phosphate ion gradually decreases with the increase of pH of standard solution, mainly because Fe-PME is mainly responsive to $H_2PO_4^-$, while the relative content of $H_2PO_4^-$ decreases with the increase of pH of standard solution, which affects the response slope. In terms of response time, we will test the standard solution of $10^{-6}-10^{-1}$ M successively for Fe-PME, and the test results are shown in Figure 5, which shows that the





response time $t_{90} < 30$ s has a relatively fast response. Then, we evaluated the service life of Fe-PME, and tested the response of Fe-PME to phosphate ion once a week in the standard solution. The results are shown in Figure S4. By the fifth week, the response curve begins to alter significantly, and this alteration is especially pronounced in the tenth week. Therefore, it can be said that Fe-PME can be used continuously for one month. Moreover, the consistency of ongoing testing is a crucial factor for evaluating the effectiveness of the ion sensor. We tested the potential of Fe-PME in 0.1 M standard solution continuously for 24 h. The potential drift does not exceed 4 mV and is mainly influenced by the ambient temperature; this is evident. The mixed solution method is chosen for selectivity evaluation, with the calculation process being as follows

$$E_{\rm ISE} = E' + \frac{RT}{n_{\rm B}F} \ln(a_{\rm B} + K_{\rm B,A}^{\rm pot} a_{\rm A}^{n_{\rm B}/n_{\rm A}})$$
(11)

There are two selective evaluation methods, the individual solution method and mixed solution method. We opted for the mixed solution approach to ensure more precise testing of reagent samples. This technique involves adjusting phosphate ion concentration in the test solution, altering interfering ion concentration, and monitoring potential changes as the interfering ions' concentration rises. Specifically, when the interfering ion concentration is multiple times that of the tested ions, the potential value will be significantly altered. For example, the selectivity coefficient of nitrate ions is -3, which means that when the concentration of nitrate ions is 10^3 times the power of phosphate ions, it will cause significant interference in the detection of the sensor. It can be seen from Table 1 that Fe-PME has good selectivity for common

Table	1. S	ele	ctivity	Coefficie	nt of (Common	Anions
Measu	ıred	by	Mixed	Solution	Meth	od	

anion	$\log K_{ m pot}$
NO ₃ ⁻	-2.9 ± 0.3
Cl ⁻	-4.1 ± 0.2
SO4 ²⁻	-4.8 ± 0.3
HCO ₃ ⁻	-3.3 ± 0.3
Ac ⁻	-2.9 ± 0.2

anions. In the actual sample test, we compared the performance of phosphate ion detection of Fe-PME with traditional UV-vis spectrophotometry (blue molybdenum colorimetry). As shown in Table 2, the actual detection concentration of

 Table 2. Real Sample Test Compared to Conventional

 Phosphomolybdate Blue Spectrometer

sample	Fe-PME (mM)	colorimetry (mM)
vinegar	1.9 ± 0.2	2.1 ± 0.1
orange juice	4.6 ± 0.2	4.8 ± 0.1
wastewater	2.3 ± 0.2	2.1 ± 0.2

phosphate ion in wine, orange juice, and wastewater is within ± 0.2 mM of the spectral method, indicating that Fe-PME can be applied in food, environment, and industrial fields. This also indicates that Fe-PME has the potential to move toward commercialization. Finally, the recovery of Fe-PME was evaluated by the addition recovery test method. As Table 3 shows, it was found that the recovery of Fe-PME was more than 96% in various common liquid samples.

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

4. CONCLUSIONS

This research project involved the creation and development of a phosphate ion sensor using iron as the base material, achieved through the electrochemical modification of an iron metal electrode. Initially, cyclic voltammetry was used to establish the necessary potential of -0.57 V for a consistent potential electrolysis. Following this, the iron electrode underwent specific modifications to elicit a reaction in the presence of phosphate ions in the solution. Analysis of the surface morphology and elemental composition of Fe-PME, utilizing SEM and EDS, elucidated its response to the phosphate ion. A two-electrode system was utilized to assess this reaction. The results demonstrate that at pH 4, Fe-PME can respond to phosphate ions in concentrations ranging from 10^{-5} to 0.1 M, with a slope of -52.8 mV dec⁻¹ and selectivity coefficients for common anions below -2. Fe-PME demonstrated positive results and efficient recovery when compared to the conventional blue molybdenum colorimetric method.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.4c02230.

Pourbaix diagram for nickel at 25 °C; response characteristics of Fe-PME in NaH₂PO₄ solution at various pHs; potential stability of Fe-PME in 0.1 M NaH₂PO₄ solution at pH 4 in 24 h; and lifetime of Fe-PME in NaH₂PO₄ solution at pH 4 (PDF)

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Notes

The authors declare no competing financial interest.

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