pH electrodes based on iridium oxide films for marine monitoring

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ABSTRACT

The pH is an important parameter that affects the growth and development of marine organisms, environmental changes, and industrial and agricultural production processes. Nowadays, important trends in pH detection and analysis are higher stability, adaptation to extreme environmental conditions, miniaturization, portability, and digital intelligence. Several studies have focused on the application of the iridium oxide film (IROF) pH electrodes in water quality monitoring and physiological analysis. The central aim of this work was to review the preparation techniques of the IROF pH electrodes and to expand their application in the field of marine monitoring. The studied methods include electrochemical deposition, electrochemical growth, sputtering deposition, heat treatment, and novel preparation methods. The IROF pH electrodes prepared via these methods are more sensitive, have a wider pH measurement ranges, and can be miniaturized further than traditional glass and pH photometer. Hence, in environmental analysis, combining IROF pH electrodes with wireless technology for the physiological and biochemical analysis of marine organisms, seawater, and sediment pore water is an important development tendency.

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1. Introduction

The pH is an essential parameter in ecological environments and biological organisms, and different pH values can influence the growth rate of cells, metabolic rates, cell division, and differentiation [1–4]. Some researchers have shown that the carbon cycles of marine coral ecosystems and even of global ecosystems are affected by fluctuating pH values, and pH fluctuations caused by wastewater discharge into upstream rivers will also affect downstream ecosystems [5–8]. Therefore, stable and continuous pH monitoring is essential in agroecology, environmental monitoring/detection, industrial production, and other fields.

In particular, due to the continuous increase in global carbon dioxide emissions, a large amount of CO_2 is absorbed by the ocean,

making ocean acidification a global environmental problem. Based on previous studies, ocean acidification will further release heavy metals deposited in the ocean sediment, reduce the calcification degree of shellfish, and dissolve the foundation of coral reefs [3,5]. The exact impacts of ocean acidification on the marine biological chain are currently not clear, requiring the use of instruments that can stably monitor the pH of the ocean.

Traditional pH glass membrane electrodes can maintain stable and accurate pH measurements in commonly used pH ranges and are still widely used. However, these electrodes have some limitations, such as large probe volumes, difficulties in miniaturization, easily damaged hydrated glass films, and high impedance and long response times under alkaline conditions [9–11]. Over the past decades, scholars have found that metal oxides such as PtO_2, IrO_2, RuO_2, OsO_2, Ta_2O_5, Ti_2O, PdO, and SnO_2 can be used to prepare pH sensors [12–14]. Compared with traditional pH glass membrane electrodes, these metal oxide pH electrodes exhibit super-Nernst phenomena and have simple and cheaper fabrication processes [15]. Moreover, using these metal oxides as pH sensing materials makes it easier to miniaturize a variety of sensor shapes [16]. Among these metal oxide electrode materials, iridium and its oxides have attracted the most attention. Electrodes based on
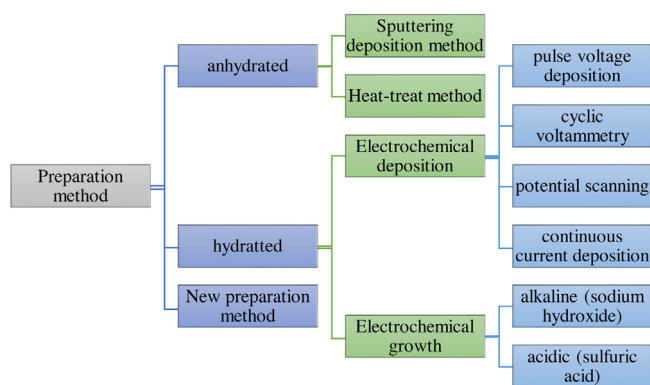
Fig. 1. Classification and summary of preparation methods of IROF-based electrodes.

iridium and its metal oxides are relatively stable and insoluble in measured solutions, but also have short response times, wide measurement ranges, high temperature (up to 250 °C) and pressure limitations, and tolerance to corrosive environments [10,17,18]. Hence, some researchers combined these advantages of IROFs to further develop the application of iridium and its metal oxide film pH electrode in specific fields. This paper will focus on the summarization of its preparation methods, research in the field of marine analysis and monitoring, and its potential application in the future.

2. Preparation of iridium oxide films electrodes

Iridium oxide films have been used in a variety of electrochromic materials, electrocatalysts, nerve stimulants, supercapacitors, and pH-sensing materials [19,20]. When used for pH sensing, these materials are mainly divided into hydrated and unhydrated membranes. The thickness and particle size of IROFs fabricated by different methods are diverse. Usually, pH electrodes prepared using electrochemical growth and electrochemical deposition are hydrated IROF electrodes. The preparation methods of the anhydrous films mainly include heat-treatment and heat-sputtering processes [19,21–24]; these methods are described in detail in Fig. 1.

2.1. Electrochemical deposition

Electrodeposition is used to deposit IROFs on various substrates, which are generally conductive materials such as lead, platinum, stainless steel, and graphite. Some non-conductive substrates, such as glass and plastics, have also been used [25,26]. Electrochemical deposition uses a complex deposition solution, and the role of each component should be considered to ensure uniformity and stability of the coating [27]. In previous works, standard electrodeposition solutions have contained $IrCl_4$, iridium

(IV) oxalate, and some other weak salt ligand ions. During electrodeposition, it is necessary to adjust the pH value of the electrodeposition solution, control the potential sweep range during deposition, and select the appropriate deposition time [13,28,29]. Common electrochemical deposition methods are listed in Table 1, which mainly include continuous current deposition [30,31], pulse voltage deposition [32], potential scanning, and cyclic voltammetry (CV) [33,34].

The requirements of the deposition solution for IROFs deposited by the above methods are different, and therefore, the allocation of deposition solution components has become critical for electrochemical deposition [22,41]. Zea et al. attempted to directly print a novel platinum nanoparticle ink to promote the adhesion of a deposited sensing material [36]. Then, a solid-state pH electrode was functionalized with anodic electrodeposited iridium oxide films on a rough nanostructured platinum-printed layer. Because it is compatible with any electrode design in the micrometer range, the design shown in Fig. 2A provides a novel intelligent wearable monitoring technology. Fig. 2B demonstrates a new IROF pH sensor based on a flexible polyimide substrate fabricated by Huang et al. The main procedure included the deposition of a 7-nm thick layer of Cr on a polyimide substrate, followed by a 0.1-μm thick layer of Au. Subsequently, the electrodes were exposed to an SU-8 sacrificial layer, and the IROF was formed by a sol-gel process [22,42]. Fig. 2C shows the IROF pH electrode at the micron level. Such IROF pH electrodes on flexible substrates are suitable for practical applications on curved surfaces and will enable numerous new applications.

2.2. Electrochemical growth

Previously, some scholars have applied a layer of iridium salt, followed by cyclic voltammetry deposition, in a method called cyclic voltammetric growth. A distinction can be made between these methods by noting that any deposition or current circulation after applying a coating applied is called an electrodeposition method. One in which the iridium wire is not coated and is directly embedded in the electrochemical cycle is an electrochemical growth method.

The IROF electrodes made by electrochemical cyclic voltammetry are commonly formed in acidic (sulfuric acid) or alkaline (sodium hydroxide) electrolyte solutions [43,44]. When pure iridium wire is electrochemically activated in an electrolyte solution, the hydrated IROFs will grow on the surface of the iridium wire [45]. Cyclic voltammetry is a simple method for preparing IROFs because it is fast and only the cyclic potential needs to be controlled and the number of cyclic scans needs to be optimized. However, the electrodes created by cyclic voltammetry have poor reproducibility and potential drift. The IROF-based pH electrodes prepared by cyclic voltammetry usually exhibit super-Nernst phenomenon, and electrode sensitivity ranges from −60 to −80 mV/pH unit [24,43,46].

Table 1
Common techniques and methods for electrochemical deposition, deposition substrates, deposition solutions, and pH response ranges.

| Substrates	Deposition methods	Deposition solution	Range of pH response	Sensitivity curve slope (mV/pH)	References
Pt	CV	$IrCl_4 \cdot xH_2O$, $C_2H_2O_4$, H_2O_2 mixed solution	1-13	-60.5 ± 5	[35]
Pt ink	Dynamic potential scanning	$IrCl_3 \cdot 3H_2O$, $C_2H_2O_4 \cdot H_2O$, K_2CO_3 mixed solution	2-11	-71.3 ± 0.3	[36]
Glassy carbon electrode	CV	Na_2IrCl_6, $PdCl_2$ mixed solution	1-5 and 6-10	-62.0 and -83.0	[37]
Ti, Au nanoparticle coated a glass	CV	$IrCl_4$, H_2O_2, $C_2H_2O_4 \cdot H_2O$, K_2CO_3 mixed solution	4-10	-70.5	[38]
Ti ring	CV	ditto	8-12	-75.0 to -83.0	[39]
Au disc	Constant potential	ditto	2-11	-74.3	[40]
$(SnO_2: F)$ glasses	anodic current density	K_3IrC1_6, K_2CO_3, $C_2H_2O_4 \cdot 2H_2O$ mixed solution	Not given	Not given	[23]
tin-doped- In_2O_3	constant current density	$[Ir(OH)_6]^{2-}$, NaOH, NaCl mixed solution	2-12	Not given	[21]
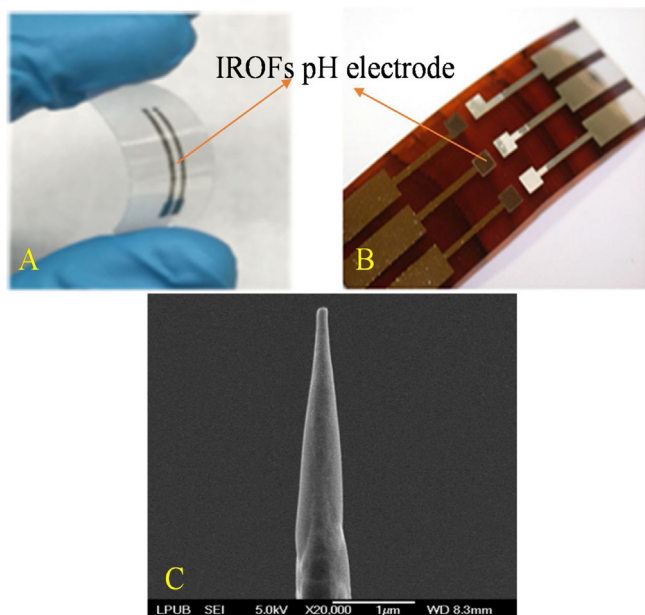
Fig. 2. Electrodeposited matrix materials with different shapes [(A) Reprinted with permission from Zea et al. (2019) Copyright © American Chemical Society; (B) Reprinted with permission from Huang et al. (2011) Copyright © Elsevier; (C) Reprinted with permission from Ndobo-Epoy et al. (2007) Copyright © American Chemical Society].

2.3. Sputtering deposition methods

Sputtering deposition, sputtering iridium salt on a substrate in oxygen or nitrogen atmosphere, called sputtering iridium oxide films (SIROFs), is also a popular method for preparing IROFs. Single crystal silicon, Al_2O_3, stainless steel, and other metallic materials are commonly used as substrates for sputtering [47,48]. The sensitivity E-pH of an electrode films manufactured by a sputtering method is generally similar to the Nernst standard value and has high repeatability. Compared with electrodes prepared by cyclic voltammetry, the stability of the electrodes potential and the interference characteristics of antioxidant reduction ions are often affected by other physical parameters (e.g., O_2, Ar partial pressure, temperature, humidity, deposition rate, substrate temperature, electric field, etc.) [48,49]. The sputtering deposition method requires relatively harsh experimental conditions and expensive equipment, leading to fewer reports using this method.

2.4. Heat-treatment methods

Compared with the other methods, a remarkable advantage of the thermal oxidation method is that IROF electrodes fabricated in this manner have long-term stability and less potential drift [50]. The thermal oxidation method requires matrix materials capable of tolerating high temperatures, since this technique requires temperatures of 300–400 °C, with some requiring temperatures higher than 800 °C [50,51]. The thermal oxidation method mainly involves $IrCl_3$ thermal decomposition, molten salt oxidation, and direct ignition of a mixture containing iridium or a sol-gel which is coated on a thermostable substrate. Then, the IROFs are formed by high-temperature oxidation [52,53]. The molten salt oxidation method involves coating nitrate or carbonate on a high-temperature resistant matrix, followed by quenching the oxide solution one or more times to form an IROF on the surface [54].

The direct burning method involves soaking iridium wire in a stable alkali solution, which quenches and oxidizes the iridium surface at high temperatures to produce the IROFs. The main distinction between this method and cyclic voltammetry under alkaline conditions is the oxidation mode. Since thermal oxidation requires high temperatures, polymeric materials and photo-impedance materials cannot be used as sacrificial oxide layers when coating a solution on the electrode matrix. At the same time, the length and frequency of burning, the oxidation temperature, and the cooling method can affect the thickness of the film and the morphology of surface particles. Furthermore, oxidation temperature and thermal oxidation time also affect the pH response time [55]. Since most IROFs obtained by thermal oxidation are anhydrous, it is necessary to complete the hydration reaction on the surface before determining the pH of the solution. Therefore, a slightly longer response time may be required. Although the electrodes prepared by thermal oxidation have excellent stabilities, cracks in the oxide film on the surface naturally occur due to the high temperatures, which reduces the service life of the electrodes [22]. Thermal oxidation and sputtering methods require high-temperature oxidation, but these also require more complex and expensive systems, significantly limiting the applications of these methods.

2.5. New preparation method

Apart from the traditional preparation methods of IROFs pH electrodes using iridium wires or other substrates, there are also relatively novel methods where nano iridium oxide is directly pressed and oxidized in an oxygen atmosphere. This method uses prepared nano iridium oxide doped with a polymethyl methacrylate (PMMA) matrix as an active sensing material for conductors and hydrogen ions. Nano iridium oxide particles are dispersed in a PMMA suspension, rapidly precipitated in water, and subsequently, the nano iridium oxide composite electrode is formed using compression molding [1]. Direct oxidation under an oxygen atmosphere oxidizes very few areas on the surface of the electrode, while the use of large-scale oxidation results in uneven and incomplete surface oxidation. Ndobo-Epoy et al. [56] covered an iridium filament surface with a poly-*p*-xylene insulating layer, while Ga used a focused ion beam to open an iridium filament vertex which was then oxidized in an oxygen atmosphere for 12 h to prepare a nanoscale IROF pH electrode.

3. Application of iridium oxide film pH electrodes

In the above, several methods of making IROFs are introduced. Each of these methods has its own advantages and disadvantages. The specific situation depends on the existing conditions and study requirements. The most important aspect is to introduce the differences between these new IROF pH electrodes and electrodes generated by traditional methods and the trend of innovative application in marine environment analysis. The relationship between IROF electrodes and its application in marine monitoring is shown in Fig. 3.

3.1. Marine organisms

Based on the miniaturization of IROF pH electrodes, pH values can be measured at specific sites for cell and physiological reactions to further understand the surface proton transfer of some crustaceous marine organisms in acidified oceans. Sensors used to measure biochemical pH values in cells should use selected appropriate matrix materials for the objects they detect and monitor. They also need to be miniaturized, typically trending to the μm-pm level, to avoid effects on the growth and biochemical reactions of biological cells. Carbon fibers are the most common matrix materials in biochemistry and physiology and simultaneously meet such high requirements. There have been several
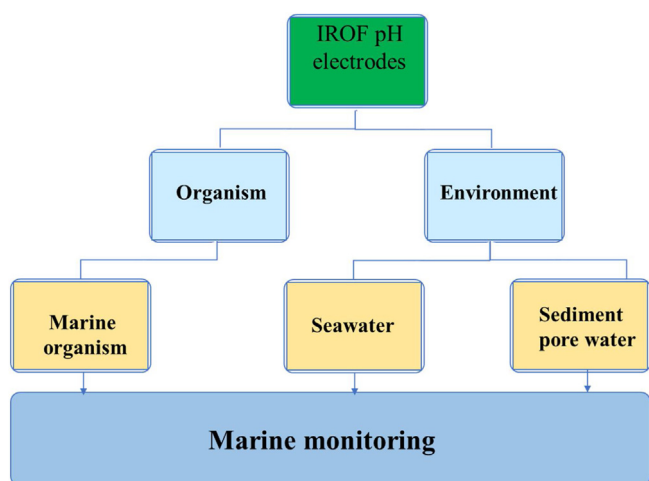
Fig. 3. Application of iridium oxide films pH sensors in marine monitoring.

excellent reviews and books summarizing the direction and application for biochemical and physiological analyses [56–58]. For example, Cork et al. inserted iridium oxide microelectrodes into the subdiaphragmatic vagus nerve of anesthetized rats, and the microelectrodes were sufficiently pH-sensitive to quickly detect changes in pH values associated with the intestinal hormone cholecystokinin (CCK) and gastric distention [59]. This work demonstrated the vital role of pH in the growth and reproduction of organisms. At the same time, the IROF pH electrode provides a new support for exploring the physiological pH fluctuation of marine organisms. Generally, the primary purpose of a pH sensor is to determine the pH of marine environments to explain and evaluate how the pH affects the survival of organisms. Based on previous studies, pH fluctuations caused by ocean acidification adversely affect the survival of calcified polychaete species [60], mussel larvae [61], and bivalves [62]. For example, Lane et al. revealed that when the pH of the metamorphic larvae of myxophora decreased, the ability of the larvae to calcify the pipeline was reduced or even lost entirely [63]. Previously, Wipf et al. prepared a pH microelectrode by depositing aqueous oxidized iridium onto a carbon fiber microelectrode which showed two linear regions of potential response between pH 2-6 and pH 6-12. The prepared electrode could monitor the proton reaction of the interface by applying a scanning electron microscope as a probe to obtain the dynamic pH change at the surface [64]. Iridium oxide microelectrodes have sufficient pH sensitivity to readily detect pH changes in their environments. Zhao et al. synthesized N-(6-aminopyridin-2-yl) ferrocene to develop a two-channel electrochemical ratiometric biosensor for local pH determination in a live rat brain, which will potentially provide a new research perspective and application scope for the IROF pH electrode [65]. Thus, we believe that the miniaturization of IROF pH electrodes can further reveal the proton transfer in somatic cells of the metamorphic larvae of myxoplasma spp. during pipeline calcification.

In addition, IROF pH electrodes can also be used to determine the pH of biological samples and tissue culture media and for real-time monitoring of pH changes in culture media to more objectively and accurately assess the biological condition of cultures [66,67]. Tabata et al. successfully monitored proton release during an amplification reaction in real-time, using a miniature pH electrode, and demonstrated the quantitative detection of nucleic acids [68]. Vanhoudt et al. reduced a μm-scale to the pm-scale by anodic polarization and protected the iridium pH electrode by cyclic voltammetry in 0.5 M sulfuric acid by placing silk in a capillary glass tube [41]. Similarly, IROF pH electrodes can also be employed to measure pH values in biological samples and tissue culture media. During ocean acidification simulations, the acidification rate of some biological cells and other indicators should be measured. In the meantime, Ges et al. generated microfluidic chips (20 μm x 400 μm) with two IROF electrodes; the acidification rate of cultured cells was obtained by a reproducible voltage difference between two IROF electrodes [69]. These multidimensional analytical methods of marine organisms using IROF pH electrodes can be used to explore the mechanism of these pH stresses to develop more targeted protective measures. There is no doubt that pH may not be the only factor affecting biological growth, but it is necessary to monitor the parameters of these potential effects through adequately designed experiments. In the future, more and more researchers will pay attention to the properties of IROFs as a pH-sensitive material when the traditional pH glass electrode cannot be used.

3.2. Seawater

The pH value is an index that must be measured during the monitoring of ecological environments and water quality because it directly determines the state of some environmental pollutants or sediments in water. A comparison of commonly used instruments for pH monitoring of marine water quality is shown in Table 2. The IROF pH electrode is not affected by turbidity and can be applied for pH monitoring in estuarine areas with high turbidity. Based on the advantages of IROF pH electrodes, it is reasonable to apply them in marine water quality monitoring. Nadappuram et al. fabricated nanoscale dual-function pH scanning ionic conductivity microscopy (SICM) probes using carbon electrodes coated with iridium oxide. By measuring the distance of the tip of the electrode, a high-resolution three-dimensional pH diagram was generated [70]. Salimi et al. did not confine their study to simply determining the pH value by the IROF electrode. Boron-doped diamond (BDD) electrodes, obtained by electrochemical deposition, were used to modify IROFs for the detection of ultra-trace amounts of environmental arsenic and mercury, which greatly broadened the applications of the IROFs electrode [71,72]. Zhang et al. applied the IROF pH electrodes prepared by an electro-growth method to determine the pH value of a marine environment, and the results were more stable than those obtained by a traditional glass electrode [73]. Using the characteristics of IROF pH electrodes to fabricate a multi-parameter integrated environmental monitoring sensor is also an important future direction for
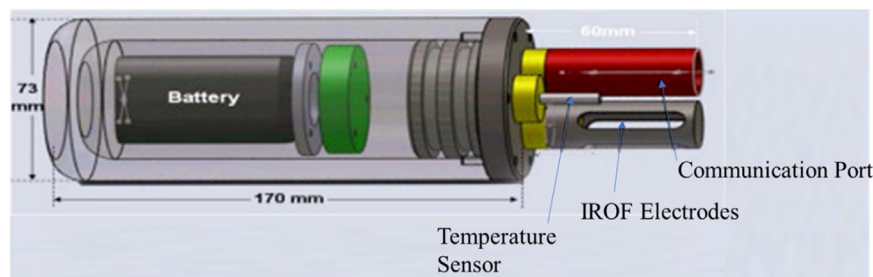
Table 2
Comparison of commonly used instruments for pH monitoring of marine water quality.

Instrument	Accuracy (pH)	pH Range	Weight (Kg)	Temperature Range (℃)	Applicable scenario
Deep SeaPHOx™ V2	±0.05	6.5-9.0	5.4	−5-45	Nearshore ocean and deep sea within 2000 m
PHBJ-260F glass pH electrode	±0.01∼0.10	−2.0-20.0	0.3	−5-105	Shallow low-turbidity water
IROFs pH electrode	±0.01∼0.10	2.0-12.0	about 0.1	10-200	Nearshore estuary with high turbidity or open sea area within 100 m
spectrophotometric pH sensor	±0.008	7.6-8.2	3.0	15-30	Aquaculture, offshore low-turbidity surface water area

Fig. 4. Scheme showing the IROF pH electrode for seawater pH monitoring [Reprinted with permission from Ding et al. (2011) Copyright © Elsevier].

environmental monitoring [74]. A multi-parameter real-time continuous water quality monitoring system has been reported by Defe et al., which can further reduce the cost and maintain high-precision measurements [75]. Wu et al. simultaneously measured the pH value, oxidation potential E_h, and H_2S concentration in a deep-sea environment using a self-made multi-parameter integrated sensor [76]; the schematic figure of the pH electrode is shown in Fig. 4. The two most important parts, the data exchange port and the integrated electrode, are presented.

Marine environmental quality data is heading towards intelligent terminals and wireless transmission. The application of IROF pH electrodes in marine environmental monitoring includes their applications in ocean buoys, which are integral parts of marine environmental water quality detection. The convenient detection of pH can be obtained through self-designed electrode shapes or assembly in electronic equipment modules, connected to a signal digital conversion system (DCS), data transmission of IROF electrode potential data, and signal processing with intelligent terminals [36]. Currently, remote data transmission is being implemented in some offshore areas, but terminal monitoring sensors are expensive. Combining IROF pH electrodes with ocean buoys can effectively reduce costs and achieve long-term monitoring of more extensive areas in seas and rivers. With the development of informationization, integrated intelligent monitoring systems based on pH and other parameters have also been developed. Ding and Ma constructed a wireless sensor network system using embedded computing, micro-electromechanical systems (MEMS), distributed information processing, and wireless communication. The system could digitize, network, and could monitor seawater quality in real-time [77]. It is also an important trend for environmental analysis to connect monitoring and analysis equipment with smart phone terminals and read data through common smart phones. Sun et al. developed a pH indicator system based on a smartphone platform, which connected to a self-made pH sensor through a headphone interface. After connection, it could be used to test and analyze sputum samples from cystic fibrosis (CF) patients [78]. By applying these technologies, real-time data transmission can be displayed on intelligent terminals, which increases the convenience of pH monitoring in these fields.

3.3. Sediment pore water

The pH value of sediment and its pore water will affect the growth and development of benthic organisms and the distribution of sediment bacteria. Current methods for determining the pH of pore water in sediments mainly include the application of glass electrodes and Raman spectrometry [79]. The application of pH glass electrodes requires a higher pore water content in sediments, and the measurement of multiple samples at intervals requires complex cleaning. Traditional pH microelectrodes consist of a glass film, and an Ag/AgCl electrode, and a saturated calomel electrode is combined to form a measurement system. Archer et al. used a

polymethyl methacrylate (PMMA) glass microelectrode to measure the pH profile of deep-sea sediments to obtain the dissolution rates of seabed sediments [80]. However, the pH glass film was damaged during tests, and the microelectrode was therefore not suitable for *in situ* measurements. The principle of determining the pH of pore water in sediments using Raman spectroscopy is based on the conjugated acid-base pair of H_2S and HS^-, whose concentration ratio is a function of pH. The Raman spectra of sulfide-containing solutions with different pH values showed regular changes in the characteristic Raman overlap peaks and H_2S. There is a particular coupling relationship between Raman spectroscopic parameters of sulfides and solution pH for the HS^- peak [81]. The main disadvantage of using Raman spectroscopy to determine pH is that the measurement range is too narrow, with values between 6.11 and 8.32 [82]. Materials based on IROF pH electrodes have more comprehensive measurement ranges and can directly measure the specific thickness of sediment *in situ*. Pore water data of different sediment layers, which are closer to the sample parameters, can be obtained. Xu et al. prepared iridium and tungsten oxide pH microelectrodes to measure the vertical profiles of sediment pH in the Xiamen West Sea and Jiulong River Estuary [83]. The pH reached a minimum at the interface of aerobic and anaerobic depths (4−5 mm) and tended to remain stable at 20 mm. In addition, the effect of S^{2-} on the microelectrode sensor was eliminated by Nafion reagent leaching.

4. Conclusions and future perspectives

In light of the importance of pH measurements, the use of iridium oxide films as pH-sensing material has emerged as a popular research topic. Numerous studies have shown that the IROF pH electrode can determine the required pH parameters easily and in-situ real-time, and future analysis and determination will not be limited to the laboratory, in contrast to the use of traditional pH glass electrodes. In this paper, we introduce the role of IROF pH electrodes in water analysis and expand their application in the comprehensive analysis of marine environments, including marine organisms and sediment pore water.

Nowadays, it is an important trend in environmental analysis to measure environmental parameters in a diversified, digital, and intelligent way. The solid-state IROF pH electrode is combined with remote wireless technology to realize the multi-parameter recording of the open sea. With electrode miniaturization, the impact of pH on marine organisms and the impact of ocean acidification on the environment and organisms can be further analyzed and evaluated.

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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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.teac.2020.e00083.

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