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Original Article

THE FUTURE OF ION SENSING: INNOVATIONS IN MINIATURIZED SOLID-STATE ELECTRODES

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Abstract: The electrochemical method, a technique reliant on the distinctions in properties among diverse substances, hinges on the detection of electrical signals within the testing detection system [1]. In contrast to conventional methods such as titration, spectroscopy, and chromatography that analyze the total concentration of ions, the ion-selective electrode (ISE) operates on a distinct principle. It converts the ion activity to be measured into an electromotive force. Functioning as potent potentiometric chemical sensors, ion-selective electrodes (ISEs) offer a range of merits, including compact dimensions, rapid response times, user-friendliness, and cost-effectiveness. They have found extensive application in environmental monitoring, industrial analysis, and clinical testing [2]. Notably, the ion-selective electrode method's detection limit remains unaffected by the sample quantity, rendering it particularly suitable for microanalysis. The innovation of the all-solid-state ion-selective electrode is a noteworthy evolution in this domain. It substitutes the conventional filling liquid in liquid-junction ion-selective electrodes with a solid-state conversion layer. This ingenious substitution circumvents the shortcomings associated with traditional liquid-junction ion-selective electrodes, such as filling liquid leakage and limited miniaturization capabilities. Contrasting with its liquid-junction counterparts that often possess a relatively large volume, the all-solid-state ion-selective electrode showcases inherent ease of integration and miniaturization. Researchers have recognized the potential of a new all-solid-state ion-selective electrode devoid of inner liquid, paving the way for innovative developments in this field.

Keywords: Electrochemical Method, Ion-Selective Electrodes (ISEs), All-Solid-State ISEs, Microanalysis, Environmental Monitoring

Original Article

1. Introduction

The electrochemical method is an analysis method based on the difference in properties of different substances, which is detected by the electrical signal of the test detection system [1]. Different from traditional titration, spectroscopy, chromatography and other testing methods for analyzing the total concentration of ions, the principle of the ion selective electrode method is to convert the activity of the ions to be measured into an electromotive force. As a potentiometric chemical sensor, ion-selective electrodes (ISEs) have the advantages of small size, fast response, simple operation, and low cost, and have been widely used in environmental monitoring, industrial analysis, and clinical testing [2]. Since the amount of sample has no effect on the detection limit, the ion selective electrode method is more suitable for microanalysis.

The all-solid-state ion-selective electrode uses a solid-state conversion layer to replace the filling liquid in the traditional liquid-junction ion-selective electrode, which avoids the shortcomings of the traditional liquid-junction ion-selective electrode such as leakage of the filling liquid and difficulty in miniaturization. Compared with the traditional liquid-junction ion-selective electrode with a relatively large volume, the all-solid-state ion-selective electrode is easy to integrate and miniaturize. Based on this, the development of a new all-solid-state ion-selective electrode without inner liquid is gradually being sought by researchers.

The current research on all-solid-state ion-selective electrodes mainly focuses on the design of the solid-state conversion layer, the material preparation of the solid-state conversion layer, and the miniaturization application of the electrode. This paper mainly reviews the application of screen printing technology, paper chip technology and microfluidic technology in the miniaturization of all-solid-state ion selective electrodes.

2. Introduction to All-Solid Ion Selective Electrode

In 1971, Cattrall et al. [3] used a platinum wire to replace the inner liquid and internal reference electrode of the liquid-junction ion-selective electrode, and then covered the surface of the electrode with an ion-selective membrane, and successfully produced an all-solid-state ion-selective electrode without internal filling. All-solid-state ion-selective electrodes without filling liquid are also called wire-covered electrodes. Due to the unstable potential response of wire-covered electrodes, researchers have started to study solid-state materials that can realize ion-electronic signal conversion, and have obtained all-solidstate ion-selective electrodes based on different solid-state conversion materials.

According to the different ways in which solid-state conversion materials exist, they can be divided into solid-contact ion-selective electrodes (SCISEs), monolithic ion-selective electrodes (SPISEs) and non-polymer membrane ion-selective electrodes (CPISEs)[4].At present, there are mainly two solid-state conversion materials based on redox reaction mechanism and electric double layer mechanism [5].The conduction process of the all-solid-state ion-selective electrode based on the conversion mechanism of redox reaction is shown in the figure(Figure. 1)below.

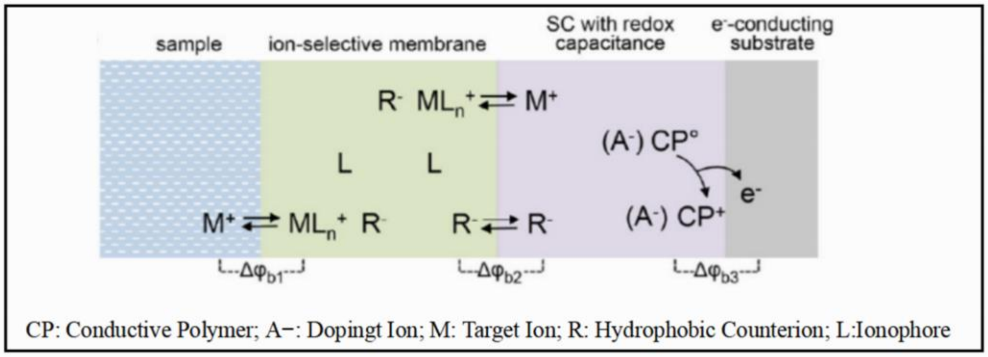

Figure 1: Diagram of conduction process of all-solid-state ion selective electrode based on REDOX reaction conversion mechanism[6]

The principle of ion-electron conversion can be expressed by the following two reactions:

$\square\ \square$ $\square e^{\square} \rightleftarrows CP^{\circ} A^{\square} M$

$CP\ A_{(solidcontact)} + M^{\square}_{(membrane)} \square_{(solidcontact)}$ $\rightleftarrows CP^{\circ}_{(solidcontact)}$

$\square\ \square\ \square\ CP\ R_{(solidcontact)} \square e\ \square R^{\square}_{(membrane)}$

The above two reactions show that the ion-electron conversion efficiency is related to the number of target ions and hydrophobic pair ions transferred. And for conductive polymer membranes doped with different anions, the transfer ratios of target ions and hydrophobic pair ions are different[6].

3. Research progress

3.1 *Miniature all-solid-state ion selective electrode combined with screen printing technology*

The screen printing technology uses a screen printing machine to directly spray conductive substances on the surface of the substrate to form a thick and non-destructive conductive substrate film layer.Musa et al.[7] prepared an all-solid-state ion-selective electrode for pH detection (Figure. 2 (a)) on a PET (Polyethylene terephthalate) substrate by screen printing. The sensitivity of the electrode is -60.8±1.7. Guinovart [8] and Zoerner et al.[9] prepared all-solid-state ion selective electrodes (Figure. 2 (b)) by screen printing for the detection of ammonium ions in sweat.Rius et al.[10] prepared an all-solid-state ionselective electrode by screen printing on a PET (Polyethylene terephthalate) plate with a single-walled carbon nanotube-octadecylamine composite as a solid-state conversion material.The electrode was successfully used for the rapid detection of potassium ions in beverages and saliva.

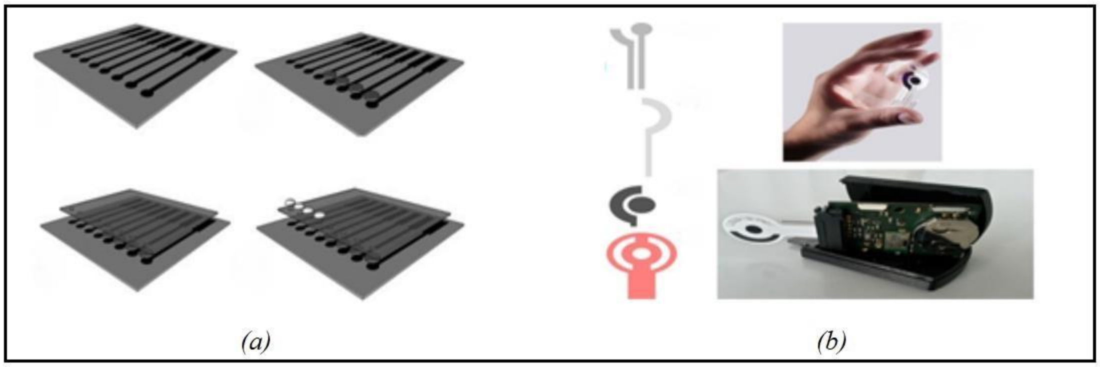

Figure 2: (a)Screen-printed electrodes for pH detection[7]; (b) Portable equipment for ammonium ion detection[9]

3.2 *Miniature all-solid-state ion selective electrode combined with paper chip technology*

Paper is considered a convenient sensor substrate due to its low cost, wide range of chemical and physical properties, and direct fluid sampling. Bouri et al.[11] developed a paper-based electrode for the detection of galactose in whole blood (Figure. 3 (a)).The filter paper sprayed with platinum layer and coated with perfluorosulfonic acid membrane was used as the indicator electrode, and the filter paper coated with conductive Ag/AgCl slurry and covered with NaCl PVB membrane was used as the reference electrode.The sensitivity of the prepared sensor is -62.8mV/decade in the range of 0.3mmolL$\cdot^{1}$~31.6mmol$\cdot$L^{-1}.Ferguson and Meyerhoff prepared a disposable paper-based all-solid-state ion selective electrode using [12] fiber filter paper as the substrate and single-walled carbon nanotubes (SWCNT) as the solid state conversion material. The electrode was successfully used for the detection of various polyanions (Figure. 3 (b)).

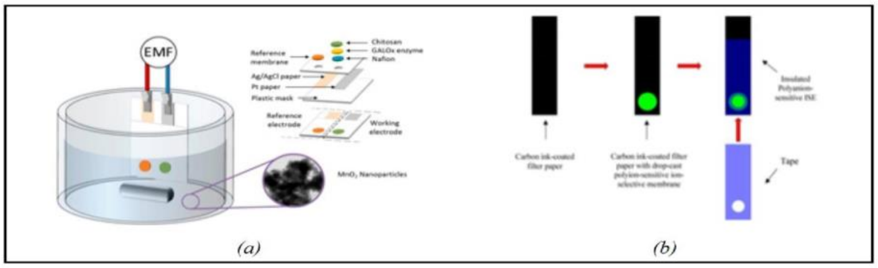

Figure 3: (a) Paper-based electrodes for the detection of galactose in blood[11] (b) Paper-based electrodes for poly anion detection[12]

Buhlmann's group[13] developed a paper-based ion detection platform (Figure. 4(a)) using colloidal imprinted mesoporous (CIM) carbon as a solid state conversion material. The final prepared all-solidstate chloride ion selective electrode and reference electrode can be used for detection in 10-fold diluted serum samples. Armas et al. [14] integrated an all-solid-state reference electrode and Na+, K+, I- ion selective electrodes on a paper tape (Figure. 4(b)).The results show that the potential drift rate of the prepared reference electrode and ion-selective electrode is larger. However, the results show that the potential drift rate of the prepared reference electrode and ion selective electrode is relatively large.

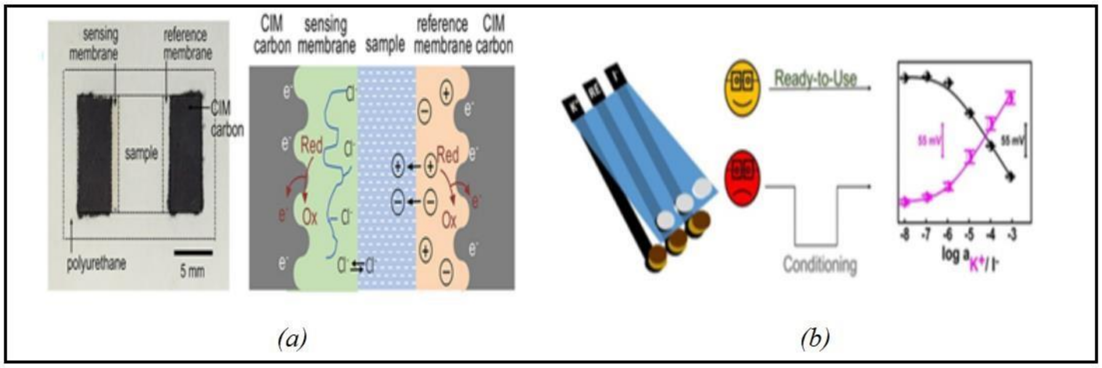

Figure 4: (a) Paper-based electrodes for the detection of Cl^{-}[13]; (b) Paper-based electrodes for detection of Na^{+}, K^{+} and I^{-}[14]

3.3 Miniature all-solid-state ion selective electrode combined with microfluidic technology

Microfluidic chips have the advantages of integration, automation, high throughput and less detection reagents.Therefore, the all-solid-state ion-selective electrode based on the microfluidic chip is easier to realize the miniaturization and integration of the sample pretreatment and analysis detection system..Min et al.[15] studied an ammonium ion detection system based on digital microfluidic technology (Figure. 5(a)), which can accurately control the moving direction and speed of droplets.The selectivity of the ammonium ion selective electrode was evaluated using the fixed interference method.The integrated ammonium ion selective electrode has a linear response in the ammonium ion solution of 1×10-6mol·L^{1}~1mol·L^{-1}, and the electrode response slope is 55.8mV/decade.Baraket et al.[16] studied a microfluidic chip (Figure. 5(b)) capable of in-situ and real-time potential measurement in flowing water for the detection of ammonium ions in solution.The chip is composed of a PDMS chip containing a microstructure and an electrode array integrated with four micro working electrodes, two micro reference electrodes and a counter electrode.

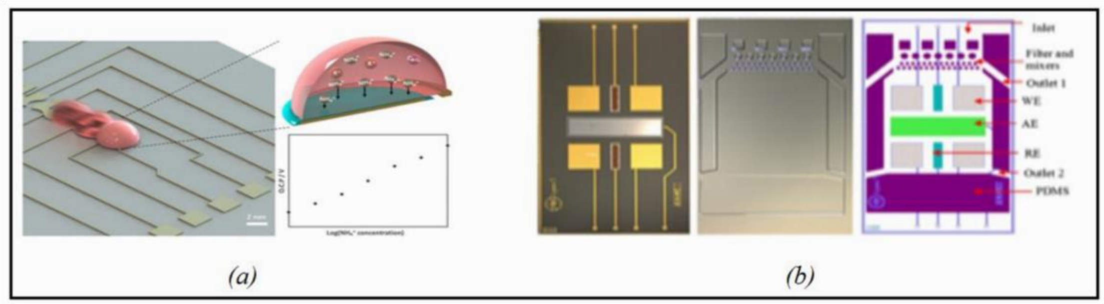

Figure 5: (a) Digital microfluidic system for NH_4^+ detection[15] (b) Detection chip for NH_4^+ in flow water[16]

Wu's research group [17] prepared a K^+, Na^+, Cl^-selective electrode array by depositing a solid-state conversion layer of PEDOT/PSS on a square gold electrode conductive substrate and coating a K^+, Na^+, Cl^-selective film(Figure. 6(a)).The test results show that the prepared electrode can be used to monitor the concentration changes of K^+, Na^+ and Cl^- in the medium during the process of cell proliferation, and the linear response range of the electrode is 1×10-3mol·L^{-1}~1×10-1mol·L^{-1}.Matzeu et al.[18] developed a microfluidic chip based on an all-solid-state ion-selective electrode for the detection of sodium ions in sweat.Gosselin et al.[19] embedded screen-printed electrodes into a microfluidic device to monitor pH changes during DNA amplification.Farzbod and Moon prepared [20] a digital microfluidic chip with an ion selective electrode array (Figure. 6(b)), which integrates the fabrication of all-solid-state ion selective electrodes, sample sampling, and sample measurement.The research shows that the detection limit of the prepared potassium ion selective electrode is 5umol·L^{-1}.

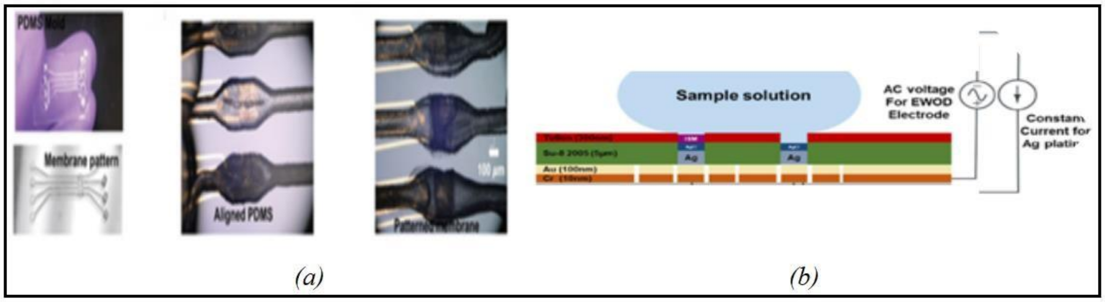

Figure 6: (a) Detection chip for ion concentration during cell proliferation[17]; (b) Digital microfluidic platform for K$^+$ detection[20]

4. Conclusions

Compared with the traditional liquid junction ion selective electrode, the all-solid-state ion selective electrode can eliminate the influence of the internal reference electrode and electrolyte, and is more conducive to miniaturization systems such as living organisms and clinical medicine.However, from the research status of the miniaturization of all-solid-state ion selective electrodes, it is not difficult to see that the development of standardized preparation technology for miniaturized all-solid-state ion selective electrodes and the research on high-throughput miniaturized ion-sensing array chips are the key to realizing real-time on-site analysis of multiple ions in the future.

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