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Stability study of Pt as reference electrode for ISFETs operating in reference electrolyte

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Abstract. Pt electrode used as reference electrode (RE) of Ion Sensitive Field-Effect Transistor (ISFET) is controversial with respect to its redox reactions with the electrolyte so that its potential can be easily perturbed by compositional changes or the flow of electrolyte. The microfluidic-controlled Pt-KCl RE system (PtRE) has been previously proposed to potentially replace the conventional RE for specific applications. This paper presents our further study on the stability of Pt electrode as ISFET's RE using the PtRE system. It is found that the potential of Pt electrode preserved in air is not stable in the beginning and drifts slowly for quite a few minutes. However, by immersing the Pt electrode in KCl reference electrolyte for a certain time prior to test, the reference characteristics of the Pt electrode can be greatly improved and exhibit as almost good stability performance as conventional Ag/AgCl electrode. Hence, Pt electrode in the PtRE system can be used as a viable alternative to conventional RE for ISFETs and other biochemical sensors.

1. Introduction

Since invented by Piet Bergveld in 1970 [1, 2], ISFET sensors exhibit a number of advantages in comparison to conventional pH-glass electrodes [3, 4]. Due to small size and fast response, ISFET devices show advantages, in comparison to conventional ion selective electrodes, of implementation in integrated circuits based on complementary metal-oxide semiconductor (CMOS) technology, especially in biomedical applications, such as detection of DNA-hybridization [5, 6], biomarker detection from blood [7], antibody detection [8], glucose measurement [9] and pH sensing [10]. As a common reference electrode (RE), Ag/AgCl RE is often used as the gate electrode of ISFETs to maintain a constant electrolyte potential. This kind of traditional RE performs its functions very well in most situations [11, 12]. Traditional RE consists of four main components [13] as depicted in Figure 1(a): metal wire, metal salt, a filling-solution reservoir, and a container with a porous membrane. Through the membrane, an effective contact between the reservoir and the electrolyte is kept resulting in a stable environment for the redox reaction between the metal and its salt. However, it is difficult to miniaturize and its on-chip fabrication presents a persistent technical challenge because of its particularity of structure.

Inert metals, such as Pt [5, 14, 15] and Au [16], have, therefore, been explored as an on-chip RE to achieve a stable potential. But the metals are by no means inert with respect to redox reactions with the electrolyte and, as such, their potential can be easily perturbed by compositional changes or the flow of electrolyte. For instance, it has been reported that a Pt wire can interact with protein and changes its own potential, which defeats a proper interpretation of the results of assay studies



performed with carbon nanotube biomolecule-binding sensors [17]. Drift in potential at the Pt/electrolyte interface is found to complicate the interpretation of the ISFET sensing outcome [18]. A follow-up study confirms that Pt is not an ideal RE [19]. Therefore, further developments of inert metal based REs for biochemical sensors are required in order to eliminate the potential drift at the metal/electrolyte interface. Based on the uncertainties of Pt mentioned above, a novel microfluidic-controlled Pt-KCl RE (PtRE) system is designed by our research team. It aims at providing a stable potential for ISFET-based biochemical sensors. In the PtRE system as shown in Figure 1(b), the Pt electrode is in direct contact with the electrolyte through a reference electrolyte of the KCl solution. With this design, the Pt electrode is independent of compositional changes, including fluctuations in ion activity or protein concentration. Our experimental results show that the Pt electrode kept in reference electrolyte in the designed microfluidic-controlled PtRE system instead of surrounded by aimed solution indeed exhibited the potential as an excellent RE. However, the stability of PtRE system need to be explored and improved for further application.

In this paper, the stability of Pt electrode as RE of ISFETs is studied through implementing it in an PtRE system on ISFET microfluidics measurement platform designed and constructed in our laboratory. We have done comparison in detail between Pt electrode and Ag/AgCl electrode. Reference characteristic of Pt electrode has been studied, and the methods to improve the stability of which have been explored. Good electrical results are obtained and verified that is effective.

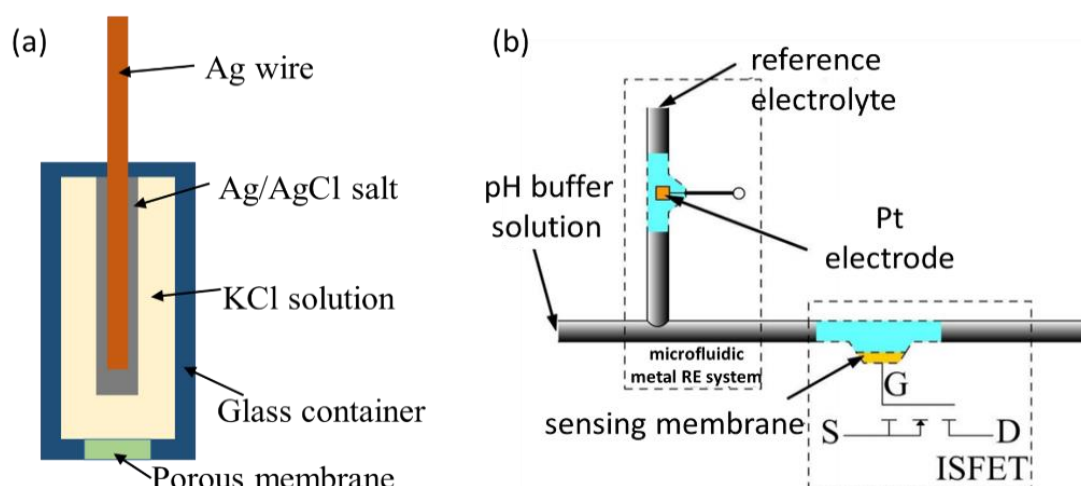


Figure 1. (a) Structure diagram traditional Ag/AgCl reference electrode and (b) Schematic diagram of ISFET system based on PtRE system.

2. Materials and methods

In the experiment, Pt electrode has been compared with commercial Ag/AgCl electrode about its electrical stability as RE in ISFET system worked on microfluidics measurement platform

2.1. Materials and fabrication

A Pt wire (CH115) and a commercial Ag/AgCl RE (CHI 111) with 3M KCl were both purchased from CH Instruments. As shown in Figure 2, the Pt wire was resealed in order to install in PtRE system to be compatible with Microfluidics measurement platform detailed below.

Commercial standard pH buffer solutions (pH7) used as analytes to test the property of our PtRE system were purchased from Reagecon. The KCl solution was used as the reference electrolyte as it is easily available and KCl has a limited reaction with Pt [20]. The KCl solution was prepared by dissolving KCl powder in de-ionized water, and its concentration was set to 1M, which should be beneficial for reduction of the solution resistance and liquid junction potential.

For ease of ISFET fabrication, a discrete commercial MOSFET (ON Semiconductor, MMFT960T1) was employed with its gate connected to a large feature-size Al_2O_3 sensing membrane fabricated on a 100-mm glass wafer in our research lab.

Microfluidics measurement platform, composed by host&slave computers, nitrogen gas cylinder, liquid and gas pipelines, a semiconductor parameter analyser (Keithley 4200-SCS), proportional valves, electromagnetic valves and other components, is designed to fulfill ISFET and REs electrical measurements.



Figure 2. Pt wire (a) was resealed (b).

2.2. Electrical measurements

The Pt and Ag/AgCl REs were installed in correct position, and the KCl solution firstly was pumped into the microfluidic channels through the reference electrolyte inlet. Then, standard pH buffer solutions were pumped in as the analytes to the ISFET system. To avoid cross-contamination between KCl reference electrolyte and pH buffer solution during measurement, the former needs to be pumped after each measurement stage in order to purge the reference electrolyte in the PtRE system. In the PtRE system, the reference electrolyte also functions as a salt bridge between the Pt electrode and pH buffer solution in order to reduce the liquid junction potential.

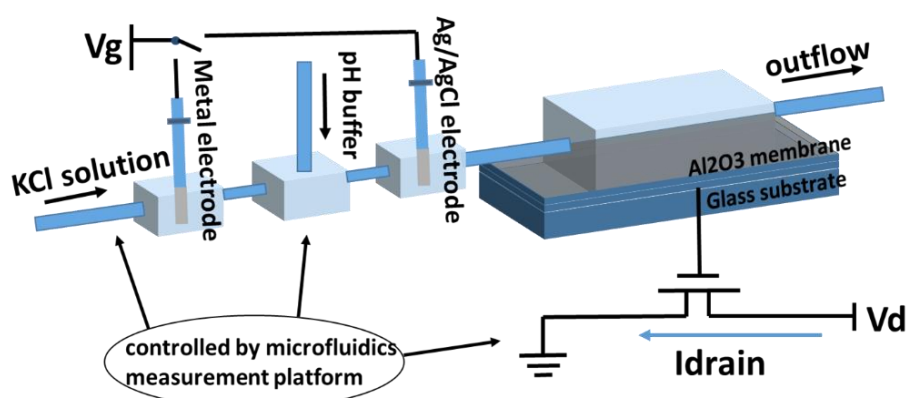


Figure 3. Schematic diagram of PtRE electrical measurements.

It is important to note that ISFET's RE is a kind of work electrode (WE) which could provide constant potential to ISFET's gate actually. To evaluate the stability of Pt electrode as ISFET's RE, open-circuit measurements and closed-circuit measurements are implemented in the setup shown in Figure 3. Open-circuit properties of Pt electrode as pure RE were measured to value its reference characteristic at a constant potential from the Ag/AgCl electrode as WE to ISFET's source at first. While in the closed-circuit measurements, the stability of Pt electrode as ISFET's RE were measured. When the potential applied to Pt electrode was kept at a constant value, the variation of drain current of ISFET indicate the stability of Pt electrode. In the measurements mentioned above, the potential applied to ISFET's RE was kept at a constant value which was chosen to bias the ISFET in strong

inversion. To minimize stochastic errors, all measurements were repeated several times on the microfluidics measurement platform at room temperature.

3. Results and discussion

In the open-circuit measurements, an Ag/AgCl electrode was set as ISFET's RE, the potential from it to the Pt RE was measured at a constant ISFET's RE-source voltage of 5 V. The measurement results as a function of time are shown in Figure 4(a). The potential increases significantly with time to approach a constant level after several minutes. This behavior indicates that the potential of the Pt electrode is not stable at the beginning but becomes reliable and stable after a few minutes. This phenomenon has been reported previously [18], and can be attributed to the presence of an initial electrochemical reaction on the Pt electrode surface. It is reasonable to deduce that if Pt electrode were immersed in reference electrolyte long enough, the stability of Pt electrode would be improved sufficiently, and the experimental data proved that it worked which is shown in Figure 4(b). The potential increases slightly with time after the Pt electrode was immersed in KCl solution for 3 days. In such condition mentioned above, the reference characteristic of Pt electrode fulfills the expected functions.

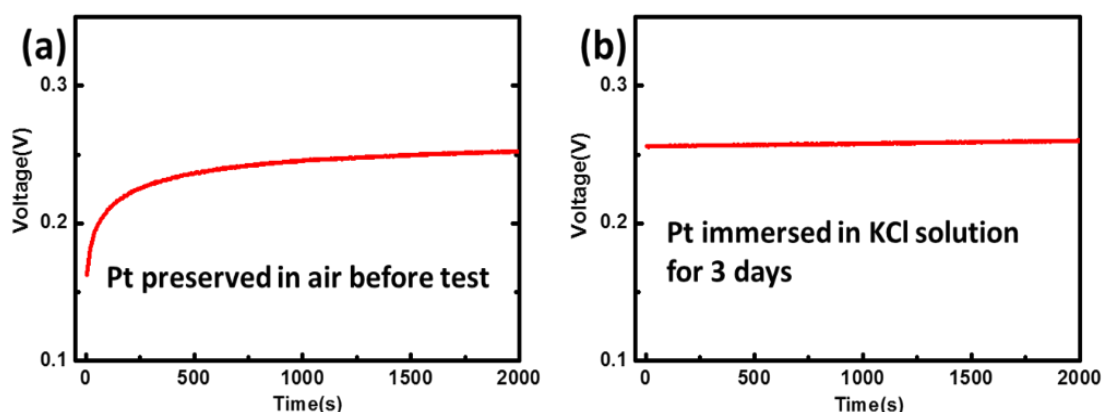


Figure 4. The potential from Ag/AgCl WE to the Pt RE as a function of time.

In the closed-circuit measurements, Ag/AgCl electrode was first applied as ISFET's RE to provide a constant potential 6 V on ISFET's gate. ISFET's drain current was measured to value the stability of Ag/AgCl electrode at a constant drain-to-source voltage of 0.1 V. Test was repeated 5 times at regular intervals, and the interval for each test was 10min. From the measurement results in Figure 5(a), Ag/AgCl electrode exhibits excellent characteristics, the repeatability error of which is as low as 0.1 mV, while the linearity is higher than 99.6%, and the response time is 2.5 s.

For comparison, Pt electrode which had been immersed in KCl solution for 3 days was applied as ISFET's RE with other experimental conditions unchanged. The measurement results are shown in Figure 5(b), Pt electrode also exhibits excellent characteristics, the repeatability error of which was 0.2 mV, while the linearity was higher than 99.6%, and the response time was 2.5 s. It indicates that the reference characteristic of Pt electrode exhibits stability performance closer to Ag/AgCl electrode and these gains were the result of stable reaction in the electrode/electrolyte interface forming liquid junction potential efficiently through immersing in KCl reference electrolyte for a certain time before test.

In order to verify the reliability of experimental results mentioned above, Pt electrode was removed from PtRE system, washed and cleaned with deionized water, and preserved in the air for 2 days. The measurement was repeated while the Pt electrode had been installed well. As shown in Figure 5(c), the first test data shows that the property of Pt electrode has degraded in some degree. The drain current increased slowly that indicated the drift in potential at the Pt/electrolyte interface because of an initial electrochemical reaction on the Pt electrode surface caused by interaction with air was significant. By the last 4 times, the response approached a stable level. However, the repeatability error was 0.6mV,

and the linearity was 99%. The stability of Pt electrode was not as well as the former test. The results suggest that Pt electrolyte preserved in air instead of immersing in reference electrolyte would cause reference performance degradation.

Based on the above experimental results and analysis, Pt electrode was immersed in KCl solution for 1 day. Then the measurement was repeated and the results were shown in Figure 5(d). The repeatability error of which was 0.2 mV, while the linearity was higher than 99.6%, and the response time was 2.5 s. The reference characteristic recovered. The results proved that Pt electrode could exhibit as almost good stability as Ag/AgCl electrode under certain conditions.

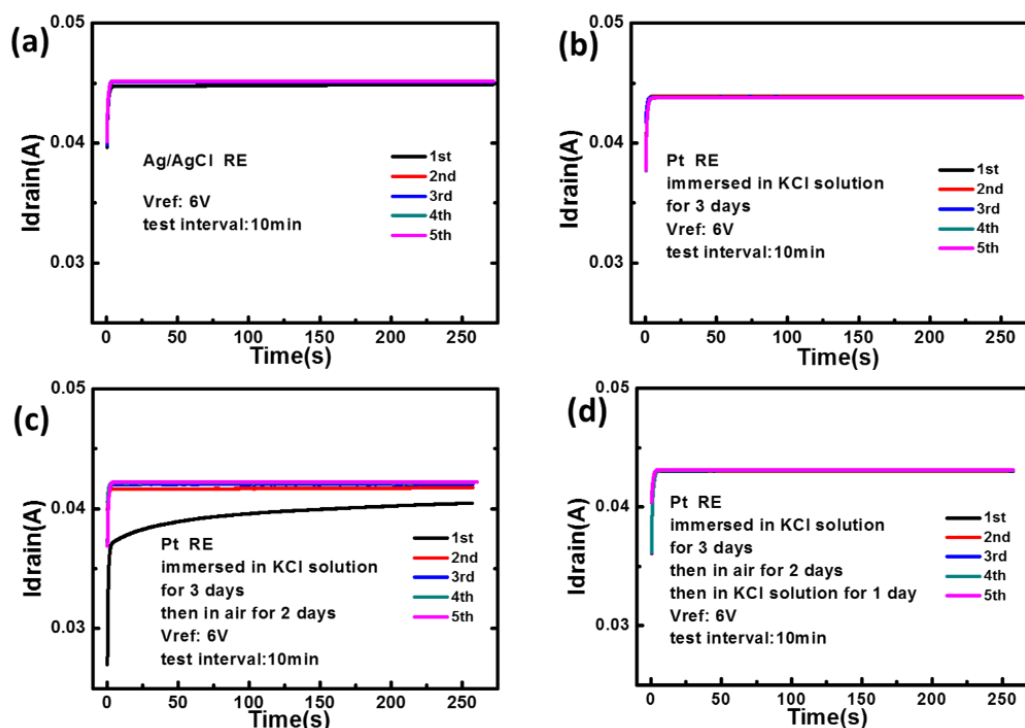


Figure 5. The response characteristics of ISFET with Ag/AgCl electrode (a) and PtRE (b), (c), (d) as ISFET's RE respectively.

4. Conclusions

In the PtRE system, a flowing KCl solution is used as the reference electrolyte to separate the Pt electrode and the analytes, so the Pt electrode can be used as an acceptable RE regardless of the variations of the analytes in the electrolyte. Based on our previously proposed PtRE system, the stability of Pt electrode as ISFET's RE was studied in this work in more detail. The experimental results demonstrate that the potential of Pt electrode preserved in air is not stable at the beginning and drifts slowly for quite a few minutes. In order to improve the reference characteristic of Pt electrode, it is necessary to immerse Pt electrode in KCl reference electrolyte for a certain time so that a stable metal-liquid junction potential can be formed. According to experimental results, Pt electrode in the PtRE system can promisingly replace Ag/AgCl electrode and provide a stable reference potential for biochemical sensors such as ISFETs for various applications.

Acknowledgments

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