

THE ISFET IN ANALYTICAL CHEMISTRY*

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Abstract

The fast chemical response of the pH-ISFET makes the device an excellent detector in analytical chemistry. The time response of ISFETs, with Al_2O_3 as the pH-sensitive gate insulator, is determined in a flow injection analysis system. Application of an ISFET and a glass electrode are compared in rapid acid-base titrations and in a coulometric system for stable pH control. Finally, a method is described that combines both the stability of the glass electrode and the fast response of the ISFET.

Introduction

The pH-sensitive mechanism of Al_2O_3 -ISFETs is based on surface reactions [1]. This leads to a very fast response compared to the glass electrode, where the potential-determining process takes place in the hydrated gel layer. This property makes the ISFET a useful detector in analytical chemistry, especially in fast automated analysis systems.

Flow injection

One application of fast pH sensors could be in flow injection analysis [2]. In this technique a sample solution is injected into a carrier solution and transported to a suitable detector. We used a flow injection system to create a stepwise change in pH in order to determine the response time of an ISFET [3]. This method proved to be very useful as it offers an uninterrupted change of solutions. The experimental set-up is shown in Fig 1.

Two buffer solutions of different pH are continuously pumped through a four-way rotary valve which selects the solution that streams into the detector block. In this perspex block the ISFET is mounted with its ion-sensitive surface perpendicular to the fluid stream, while a reference electrode is placed downstream.

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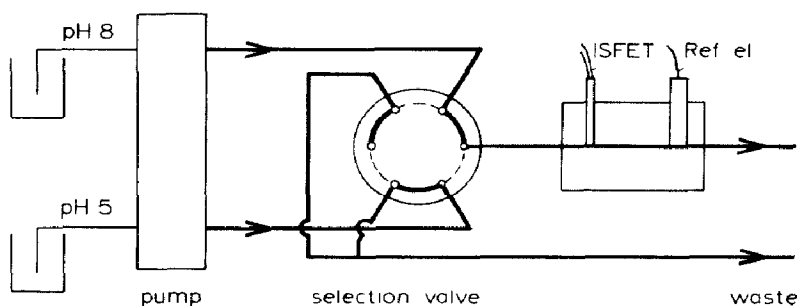


Fig 1 Diagram of the experimental set up to determine the response time of an ISFET

Of course, the response time of the system depends on the steepness of the pH gradient that is offered to the detector. We found that this response time depends on the composition of the two buffer solutions. When two solutions of approximately the same buffer capacity are used, the response time is considerably higher than in the case where the second buffer has a greater capacity, thus reducing mixing effects of the solutions. The relationship between response time and inverse flow rate is shown in Fig 2

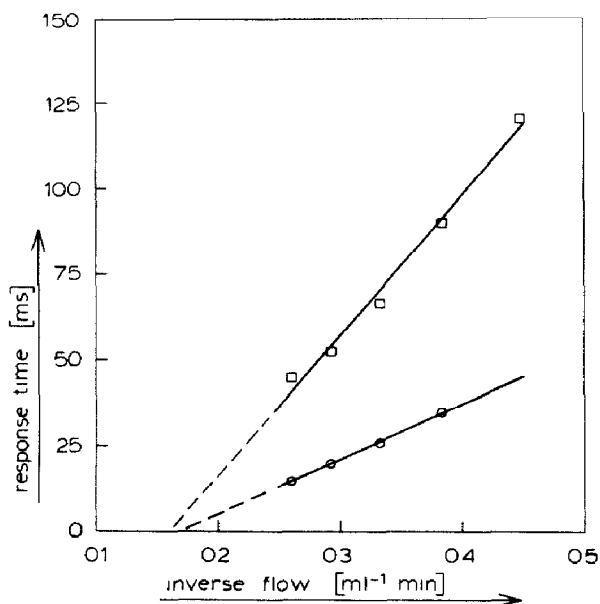


Fig 2 Response time of an Al_2O_3 ISFET. The initial pH is defined by a pH 8 buffer by Merck (\square). Second solution is a buffer by Merck, pH = 5, buffer capacity $\beta = 0.03$ (\circ). Second solution is a 1M acetic acid/1M sodium acetate buffer, pH = 4.7, $\beta = 1.15$.

Since this linearity is valid for both combinations of buffer solutions, it suggests that the response time of the system is not determined by the electrode nor by diffusion through the stagnant layer at the electrode surface. The limiting factor is here the non-ideality of the stepwise pH change.

Extrapolation of the linear relationships in the Figure makes it probable that the intrinsic response speed of the Al_2O_3 -ISFET is at least of the order

of 1 millisecond. This experiment justifies the assumption that the response mechanism is based on surface reactions rather than on diffusion-limited changes in the bulk of the surface insulator.

Fast titrations

The speed of automated acid–base titrations is normally limited by the slow response of the glass electrode. Use of an ISFET as a pH monitor permits titration speeds that are considerably higher.

We studied the titration of tris(hydroxymethyl)amino-methane (Tris) with hydrochloric acid [4]. Experimental results with a glass electrode and an ISFET are shown in Fig. 3. Allowing a 1% titration error, we see that this limit is reached at a speed of 1 ml/min for the glass electrode. Using the ISFET, overshoot is below 1% even at the highest titration speed of 5 ml/min. The limiting factor in the latter case is again not the pH sensor but the mixing of the solution. This is shown in the lower curve of Fig. 3, where stirring was improved by mounting two glass strips on the wall of the titration vessel, causing better turbulence.

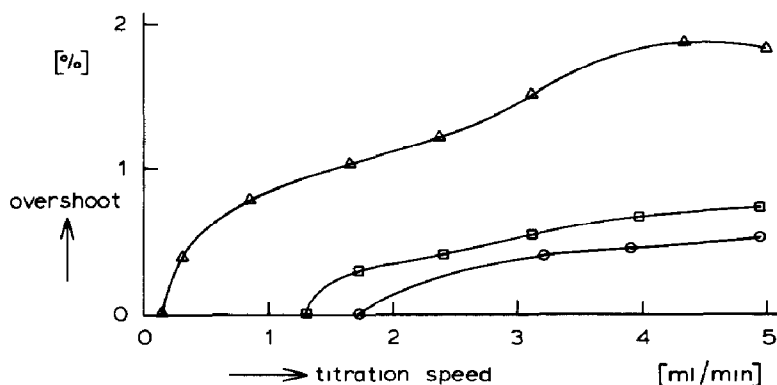


Fig. 3. Overshoot in the titration of 0.5 mmol Tris with 0.1000 M hydrochloric acid: (Δ) Glass electrode, (\square) ISFET, (\circ) ISFET with improved stirring.

Coulometric control system

We designed a coulometric control system in order to achieve accurate control of the pH in an unbuffered solution [5]. This method ensures control of a constant pH or desired pH gradients without altering the total volume or ionic strength of the solution. The dynamic properties of the control system are determined by the stirring of the solution and the response time of the pH sensor. Therefore the use of an ISFET is again favourable compared to a glass electrode.

The system (Fig. 4) controls the pH of a certain volume of solution. Its pH is measured and fed into a micro-computer where it is compared to a desired pH value. Deviations between actual and desired pH are corrected by

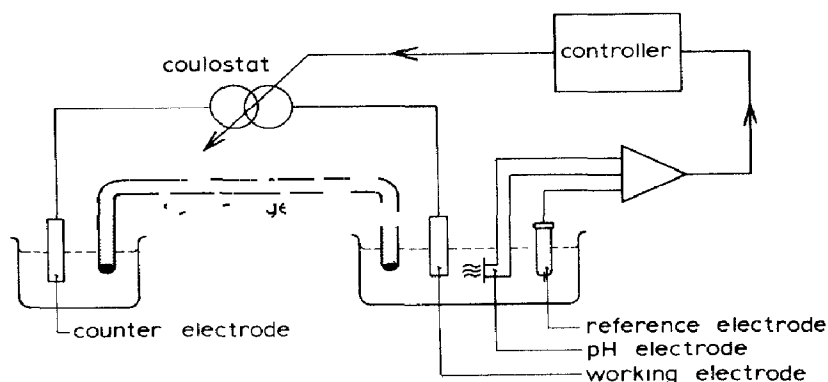


Fig 4 Experimental set up of the coulometric control system

coulometric generations of protons or hydroxyl ions by means of the hydrolysis of water. A stable and rapid operation of the system requires that the design complies with certain control engineering criteria. In contrast to the titration example, we now consider rather small changes in pH. This allows us to linearize the response of pH to reagent addition over small regions, thus facilitating the description of a model. Our description of this model contains four different time constants. Two of these are caused by the transportation lag and mixing of the generated ions in the solution. The pH is sampled once every second, introducing a delay of half this sampling interval.

The fourth time constant is due to the pH electrode and its accessory amplifier. In the case of the glass electrode this time constant is about 3 seconds, but for the ISFET it is so small that it can be neglected.

The difference in response time of the electrodes allows a closed-loop amplification of the system which is, in the case of the ISFET, twice as high as for the glass electrode. This higher amplification results in a faster and more stable pH control, as can be seen in Fig 5. This Figure shows the recovery of the system to pH 7 after addition of a drop of 0.01 N hydrochloric acid.

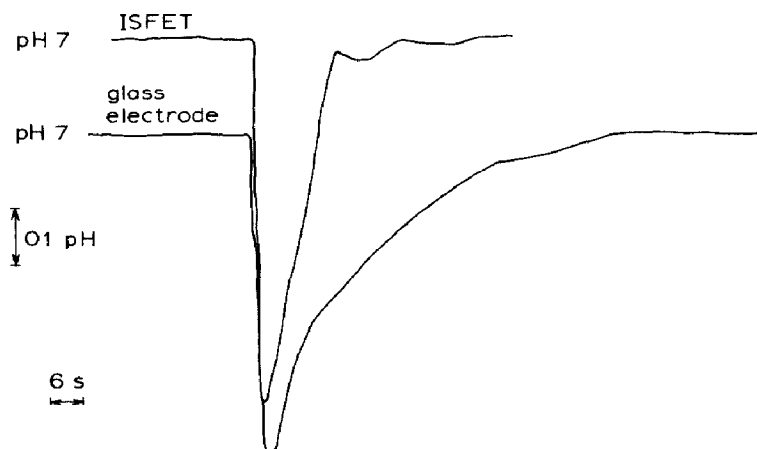


Fig 5 Recovery of the pH after disturbance by injection of 0.03 ml 0.01 N HCl

Parallel operation of a glass electrode and an ISFET

Although the ISFET is a very useful sensor in analytical applications, it is inferior to the glass electrode when long-term stability is considered. Modern glass electrodes drift as little as 0.002 pH/day, whereas ISFETs can show a drift of about 0.5 mV/h or approximately 0.1 pH/day. The causes of this drift are not yet fully understood.

To get the best of both worlds, we constructed a pH measuring system that combines the favourable properties of both the glass electrode and the ISFET. The signals of the two electrode amplifiers are summated after filtering. From the glass electrode we take only the low frequency portion of its response, while the ISFET adds the higher frequency components of a given change in pH.

We use simple first-order filters that can be easily matched to give an over-all linear frequency response. To obtain the correct pH reading at the output of the system, the sensitivities of both electrode amplifiers have to be matched. The d.c. level of the output is provided by the glass electrode-pH meter, which is calibrated against two standard buffer solutions. The offset of the ISFET amplifier is not important since it is blocked at the high pass filter. Figure 6 shows a schematic diagram of the system as well as a typical output registration. The dashed line in the Figure represents the corresponding output from the glass electrode only.

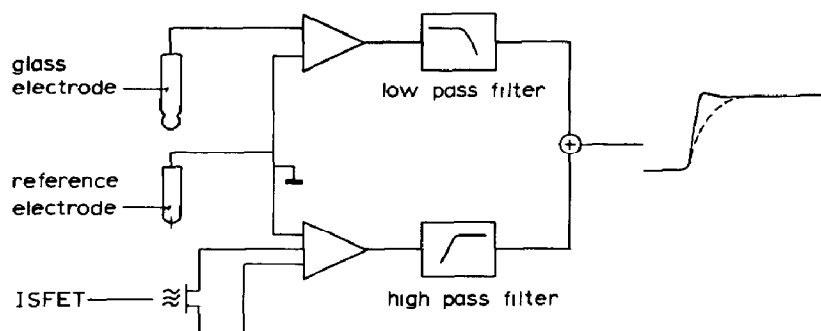


Fig. 6 Parallel operation of a glass electrode and an ISFET, together with a typical output registration. — Glass electrode + ISFET — — — Glass electrode only

Conclusions

Summarizing the results of the various experiments described in this paper, it can be said that the pH sensor need no longer be the limiting factor when it comes to speed of analysis. Further improvement can be expected from better mixing of the solutions, for instance through miniaturization of the various experimental set-ups. Here the ISFET offers excellent possibilities because of its small dimensions.

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