Investigation of Repeatability of Sol-Gel Iridium Oxide pH Sensor on Flexible Substrate

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ABSTRACT

In this paper, we presented the fabrication process of miniature pH sensor arrays on flexible polymer substrates. The repeatability of the sensors based on sol-gel fabrication processes was investigated. The sensor repeatability was characterized with linearity, decay time, environmental parameter control and potential stability. Similar linear responses were found in different batches of sensor arrays. Near super-Nernstian responses were measured on each sensor with slope ranges from –71.6 to –110 mV/pH within a pH range between 2 and 12. The response times were compared in different batches. Six to twenty five seconds of average decay time were shown in each sample repeatedly. Three sensors showed the close potential response in different volumes of pH buffer solution. The sensor showed good stability in each step of the titration process between pH values of 1.8 and 11.9. The peak and saturated potential values presented high correlation with pH values with minor noises. The results showed good sensitivity, stability and repeatability using the sol-gel processes for iridium-oxide pH sensors on flexible substrates.

Key words: miniature pH sensor, sol-gel process, linearity, decay time, environmental parameter control, potential stability

INTRODUCTION

Although the glass membrane pH electrodes have been used in wide range of applications because of the good sensitivity, selectivity, stability and long lifetime [1], the fragility and physical size features of glass electrodes still restrict the applications on in vivo biomedical, clinical and food monitoring. To target at those applications, the different kinds of miniature pH sensor such as ion-sensitive field-effect transistor (iSFET) pH sensors [2,3], optical fiber pH sensors [4,5], hydrogel film pH sensors [6] and solid-sate pH sensors [7,8] were investigated and demonstrated. However, most of those sensors were still built on rigid substrate such as silicon wafer or glass slide. The non-deformable pH sensors cannot be used for certain *in vivo* environment such as the neuronal implants [9,10]. Therefore, the polymer-based substrate [11] was chose and applied on the fabrication for the next generation pH sensor.

In our previous paper [12], we presented the use of sol-gel technique for the preparation of iridium oxide (IrO$_x$) pH sensing film on flexible Kapton substrate. The solid state IrO$_x$ film was formed by sol-gel technique, dip-coating [1,13], and thermal oxidation [14] processes.

In this paper, we presented the continuation of our previous work [12]. We demonstrated the repeatability, reproducibility, and stability of our pH sensor fabrication by the tests of linearity, time response, different volume, and step potential responses. The parameters including the metal thickness, sol-gel agent ratio, annealing temperature, and time of electro-plating on different fabrication batches were fixed in order to examine the repeatability and reproducibility of the fabrication process of our pH electrodes. Large- and small-volume tests demonstrated the stability of pH sensor performing in different environment condition.

The present paper showed the robust performance of our flexible pH sensor made by the simple IrO_x sol-gel and AgCl electroplating methodology.

SENSOR FABRICATION

The pH sensor structures were formed on a flexible Kapton polyimide substrate. All metal layers were deposited by electron-beam evaporation. Photolithography and lift-off processes were applied in the fabrication procedures.

Anodic Electrode Fabrication Procedure

Metal deposition: A layer of 70-Å thick Cr was deposited as an adhesion layer of the 1000-Å thick Au layer as show in Fig.1 (a).
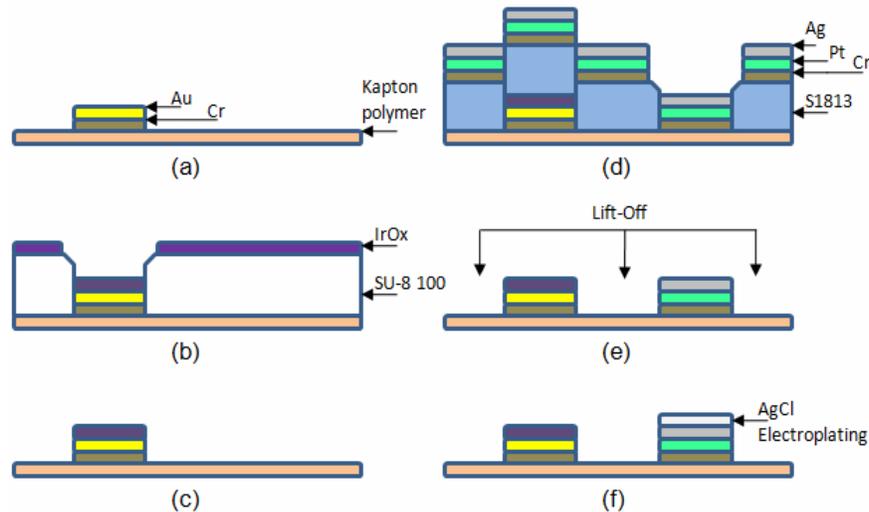
Figure 1 Fabrication processes: (a) Cr and Au deposition, (b) $IrCl_4$ sol-gel process after SU-8 deposition as the sacrificial layer, (c) lift-off process result, (d) Cr, Pt and Ag deposition with S1813 as the sacrificial layer, (e) lift-off process result, and (f) AgCl electroplating.

Sacrificial layer: A 100 μm thick SU-8-100 photoresist layer was coated as shown Fig. 1(b) to be a sacrificial layer for IrO_x sol-gel process. The SU-8 layer defined the sensing area on top of the Au layer.

IrO$_x$ sol-gel process: The sol-gel coating agent was based on the recipe described in [12,14]. The solution was stirred continuously for at least two hours with a magnetic rod. A thin layer on the flexible substrate was formed by dip coating at a 2 cm/min withdraw rate by hand holding.

Thermal treatment: The sample was baked at 120°C for 15 minutes on a hot plate right after the dip coating process, and SU-8 layer was stripped off after baking. The sample was treated in an oven with a heating profile described in [12]. The surface needed to be treated at a temperature between 300°C and 350°C [15] to obtain an amorphous iridium oxide thin film.

Cathode Electrode Fabrication Procedure

Metal deposition: 70-Å thick Cr was deposited, followed by a 60-Å thick layer of Pt as an adhesion layer for the Ag layer. A 3000-Å thick Ag layer was deposited using the electro-plating process on top of the Pt layer as shown in Fig.1 (d).
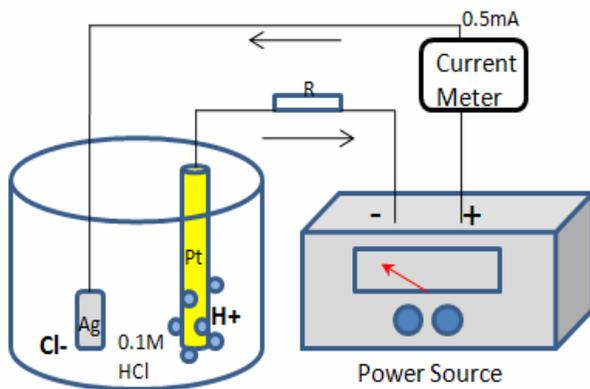
Figure 2 Electroplating setup for the AgCl reference electrodes.

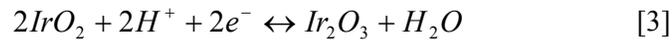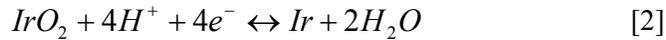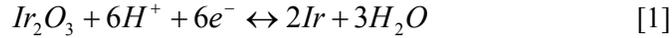**Figure 3** The PDMS polymer enclosure around the flexible pH sensor.

AgCl electro-plating: Electrochemical anodization process was used to obtain the silver chloride (AgCl) reference electrode same as the description in [12]. A brown silver chloride (AgCl) layer was formed on the silver surface. The electrodes were saturated in potassium chloride (KCl) [12,16]. Fig. 2 shows the electroplating setup for the AgCl reference electrodes.

PDMS Enclosure

PDMS polymer was made in a 10:1 ratio by weight of SYLGARD 184 and curing agent [17]. The mix was cured on a 70°C hot plate for 24 hours. The 0.2-cm thick PDMS layer was then bonded on the sensor surface with a well of 0.1 cm^3 volume to confine pH buffer solution on the pH electrodes for measurements shown in Fig. 3 and Fig. 4 (b).

THEORY

The iridium oxide (IrO_x) and silver chloride (AgCl) were used as sensing and reference electrodes, respectively. A pH-dependent redox equilibrium of two materials generated potential difference when pH was changed. There are three possible mechanisms on pH-dependent redox equilibriums between two oxidation states of IrO_x. The pH potential sensitivity will be –59.16 mV/pH regarded as the Nernstian potential response [18-20].

$$Ir_2O_3 + 6H^+ + 6e^- \leftrightarrow 2Ir + 3H_2O \qquad [1]$$

$$IrO_2 + 4H^+ + 4e^- \leftrightarrow Ir + 2H_2O \qquad [2]$$

$$2IrO_2 + 2H^+ + 2e^- \leftrightarrow Ir_2O_3 + H_2O \qquad [3]$$

$$E = E^0 - 2.303\frac{RT}{F}pH = E^o - 59.16\,pH \qquad [4]$$

MEASUREMENTS

In this paper, we aimed to demonstrate the repeatability of our pH sensors fabricated in different batches. Fig.4 (a) shows the measurement setup for our flexible pH sensors. An NI-DAQ 6008 USB card with a LabVIEW program was used for analog potential recording. A commercial Hanna pH meter was used to verify the pH values of solutions. The contact pads of the pH sensor were coated by silver epoxy in order to have good conductivity for the connection between the sensor and the DAQ card. A thin layer of PDMS was coated on top of the silver epoxy as shown in Fig. 3 for isolation when pH sensor was immersed in the test solution.
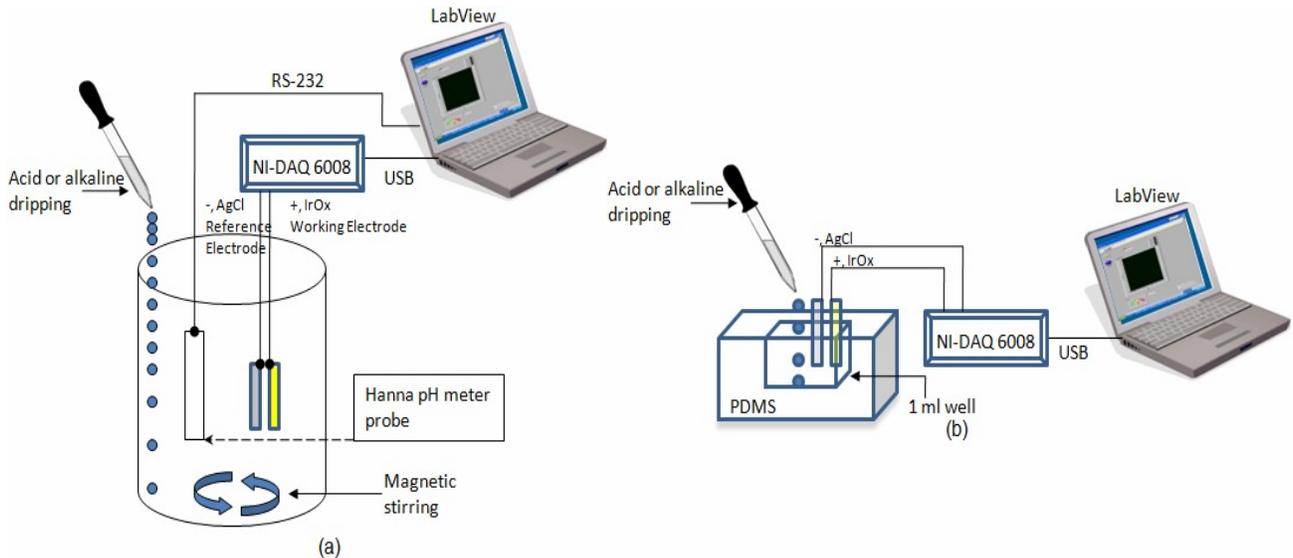
Figure 4 The pH titration and measurement setups for (a) large and (b) small volumes of solution.

Titration test: The sensor was immersed in acid or alkaline based diluted solution stirred with a magnetic rod in the beaker. We used hydrochloric acid for acidic titration tests. NH_3 and KOH were used for alkaline titration tests. The Hanna pH meter was placed in the solution and connected to its signal processing card. Both the potential from our sensor and the pH level from the Hanna pH meter were recorded in a computer simultaneously.

Small volume test: The pH 2, 4, 6, 10 and 12 buffer solutions were dropped into the 0.1 ml well individually to test the sensor performance. The sensor was rinsed by DI water between each test.

Large volume test: The sensor was immersed in 450 ml of pH 2, 4, 6, 10 and 12 buffer solutions individually in the beaker. The sensor was rinsed by DI water between each test.

## RESULTS AND DISCUSSION

Linearity Performance

The reproducibility and repeatability of our fabrication process can be obtained by measuring three electrodes from different batches of identical fabrication process. Three linear potential responses of the three IrO_x pH sensors were confirmed by pH titration tests. KOH was dripped into diluted HCl based solution for titration. Shown in Fig. 5, the pH sensors from three different fabrication batches demonstrated near linear super-Nernstian responses [20] with similar sensitivities of –71.6 mV/pH, –81.7 mV/pH and –110 mV/pH from pH=2 to pH=12 at 25°C. The variances of these three linear responses were 0.032, 0.018, and 0.02, respectively. These three sensors all performed better than the –59.16 mV/pH super-Nernstian's sensitivity [18]. These sensitivity responses demonstrated good reproducibility in our fabrication process. The 10 to 30 mV of sensitivity deviations between sensors may be due to different oxidation state as described in [22,23].
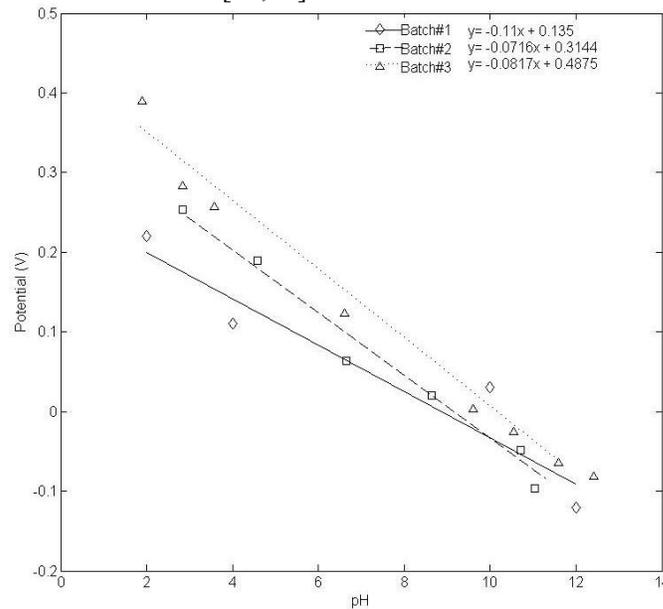
Figure 5 Linear potential response for pH sensors from three batches. The tested pH ranges from 2 to 12.

Response Time Performance

Titration tests were performed to investigate the response time of our pH sensors. A rapid step change in pH level was represented by quickly adding a certain amount of HCl solution into alkaline-based solution or adding KOH solution into acidic solution. The response time is defined as the time required to reach 90% of the equilibrium value [21]. Fig. 6 shows the results of the pH sensors from three different fabrication batches with the transition steps of pH changing from pH=1.8 to pH=8.4 and from pH=5.6 to pH=2.0. The response times ranged from about 6 to 25 seconds, which also included and depended on the different mixing time of the dripped liquid with the base solution during titration processes. The localized mixing dynamics of liquid is difficult to control, however. These three sensors all showed similar and reasonable time responses during the titration, both from the acid to alkaline transition and alkaline to acid transition. This result not only presented good sensor reversibility, but also good reproducibility and repeatability.
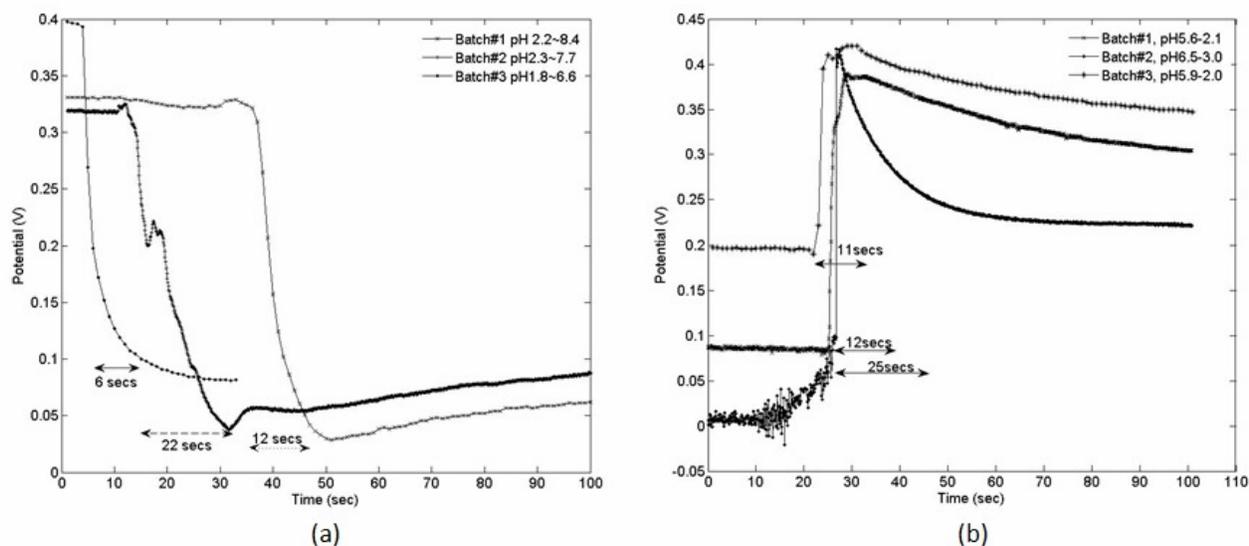
**Figure 6** Response times of our pH sensors from (a) pH=1.8 to pH=8, and (b) pH=5.6 to pH=2.

Environment Parameters

Fig. 7 demonstrates the potential responses with two different volumes of pH buffer solutions for the pH sensors from three different fabrication batches. 0.1 and 450 ml pH buffer solutions were used as the small and large volumes. Three batches of the pH sensors showed close potential responses in the small volume tests of pH= 2, 4, 6, 10 and 12 buffer solution. The 3rd batch pH sensor was tested in the large volume pH buffer solutions. Both in small and large volume tests, the pH sensors showed similar linear responses and clear identification of different pH levels. In the experiment, the large volume of buffer solution produced higher potentials than the small volume buffer solution did at the same pH levels. This may be due to much more hydrogen ions in the large volume of liquid than in the small volume. With the mechanism of our pH sensor, the sensing potential depends on the pH value, which is the log value of the activity of the ion numbers. In this ion-selective pH sensor, it responds to the potential created or released

by the active ions in the solution. Therefore, when the ion source is low, the potential will not reach the same level as the solution with higher ion strength does. The ion reduction also causes the result of slow response time resulting inaccurate pH measurements [24].

Potential Step Responses

Fig. 8 shows potential responses of two IrOx sensors to pH changes in a series of five different pH levels. The diluted HCl-based solution was titrated by KOH dripping from pH=1.8 to pH=11.9. Two sensing potentials responded to the pH level changes quickly when the titration started. This experiment demonstrated the dynamic testing of sensors from two different fabrication batches. The result showed that the response transients of two electrodes were almost identical with the titration steps. The deviation of potentials may be due to the oxide states as described in [23]. The higher potential responds to higher valence oxide and vice versa. The oxidation state is determined by the composition of IrOx film that can vary the potential shift at the same level of pH [23]. This experiment showed good stability of our sensors, and good reproducibility of the sol-gel fabrication processes.
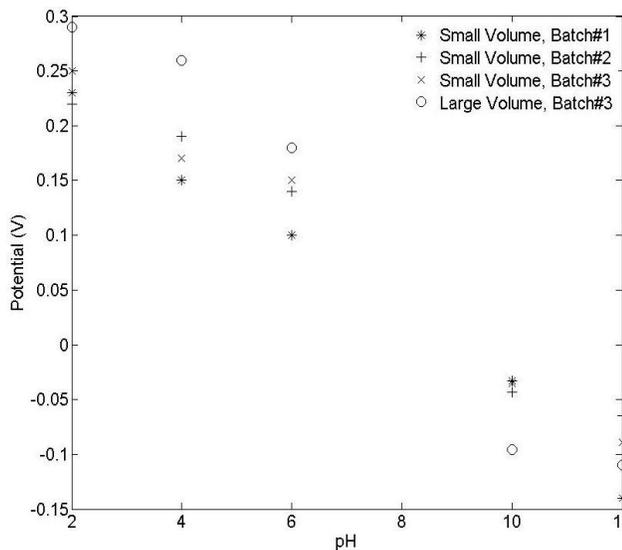
Figure 7 Large and small volume environment results.
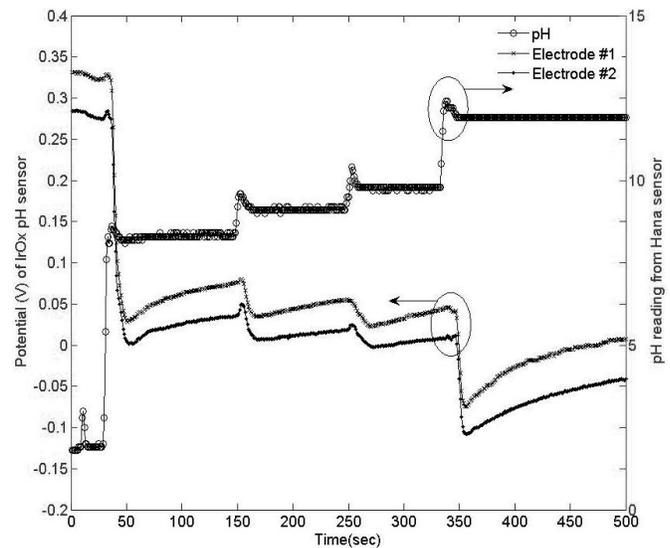
Figure 8 Potential responses in titration experiments.

CONCLUSIONS

This paper presented the repeatability, reproducibility, and stability of an IrO_x pH sensor fabricated on a flexible substrate. The sol-gel process was repeated in the different batches of fabrication process. Three different batches of pH sensors showed similar near super-Nernstian response which ranges from −71.6 mV/pH to −110 mV/pH as reproducible sensitivity in our fabrication process. These sensors demonstrated good reversibility, and similar response times to show the good reproducibility and repeatability in our fabrication process. Different volumes of fluid and step potential tests demonstrated good stability with three different batches of pH sensors. However, some potential deviations happened in the experiments. It

may be due to the issues associated with the space charges, oxidation state, and film hydroxylation. Those phenomena maybe caused by the porous distribution, thickness, and surface properties of the IrO_x thin film. With respect to the surface factors and different redox reactions occurred and related to changes of the pH charging potential, the fabrication quality control in the thickness and crystal structures of IrO_x film is very important during the fabrication processes.

ACKNOWLEDGEMENT

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