Research note

An innovative electro-corrosion recess creation technique for improved microelectrode fabrication

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Abstract

A new and simple electrochemical (corrosion) method for recess creation for the fabrication of metal and metal–metal oxide microelectrodes has been developed. Controlled recess was created in low melting point alloy (LMA)-filled micropipettes using slightly acidic 1–3M ZnCl₂ as the electro-corrosion solution. The current was applied from a 3 V DC source. The recess length in the LMA-filled micropipette can be manipulated as needed for a specific microelectrode by varying the electro-corrosion time. The present method is expected to make microelectrode fabrication a less tedious process. Dissolved oxygen, oxidation–reduction potential and pH microelectrodes have been made using the present method and the microelectrode characteristics were found to be in conformity with those reported by other researchers.

Keywords: Microelectrode; Low melting point alloy; Recess creation; Electro-corrosion

1. Introduction

Microelectrodes are powerful tools for micro-scale measurements in physiology, neurology, medicine, microbial ecology, and environmental studies. Because of their specific properties along with their sturdy nature, metal and metal–metal oxide microelectrodes are often used to study micro-scale environments and to measure concentrations and profiles of parameters such as dissolved oxygen (DO), oxidation–reduction potential (ORP), pH, membrane potential and current in various test materials.

Currently, there are two most accepted methods to make metal and metal–metal oxide microelectrodes. The first method is to taper a metal wire (such as platinum or iridium) and then shield the metal wire with a glass micropipette (Method 1). The second method is to fill a glass micropipette with an alloy (e.g., low melting point alloy (LMA)) (Method 2). Usually, the surface of the metal wire or the alloy in the glass micropipette is then plated with another material (e.g., metal or metal oxide) so that the microelectrode can be used as a working probe. Oxygen microelectrodes are normally made by plating gold [1–3]. Gold plating is also used for the fabrication of glucose microelectrodes [4]. Silver is plated for chlorine or S²⁻/C⁰ microelectrodes [5,6], iridium oxide for pH microelectrodes [7], and platinum for ORP microelectrodes [8].

In the first method (using a tapered wire) it takes a long time and effort to obtain the desired shape and diameter in the metal used. In addition, it is difficult to perfectly shield the metal wire with the glass micropipette; gaps often exist between the metal wire and the glass micropipette making larger metal surface area exposed to the test material which considerably impairs the performance of the microelectrode [9]. It is often difficult to control the tip diameter in such a microelectrode [3]. When a recess needs to be created in such a metal microelectrode, it can be done by using an electrochemical method with KCN [2,6] or H₂SO₄ [7] as the corroding solution.

On the other hand, the second method (using LMA), though comparatively easier, has its own limitations.
Not every LMA is suitable for use [6]; the alloy should have very low expansion as it is allowed to set after melting inside the micropipette [1]; otherwise cracks may develop in the glass micropipette. If a recess is needed, as in the case of a DO microelectrode, it is difficult to control the length and the diameter of the recess even when a glass beveller is used. Ability to create a recess absolutely depends on the skills of the person working on it. The failure rate is very high even with an experienced person. The recess is very often too long or too short when recess is created by the conventional method of ‘heating and pushing’ the LMA inside the glass micropipette [1,10]. Reheating may also create cracks and gaps in the alloy. The cracks and gaps may be removed by heating and pushing the alloy again, but that may be at the cost of the already created recess. While the recess creation is a very difficult art, successful creation of a recess does not ensure a stable microelectrode after electroplating. Normal success rate in stable microelectrode fabrication is ~ 20%. Linsenmeier and Yancey [1] reported a success rate of about 40% in recess creation (not stable electrode fabrication!). They suggested that several factors influence the success of this procedure, including the shape of the glass, the position of the glass in the filament used for heating, and the filament temperature. So far recess creation has remained an art rather than being a science.

This paper describes an electrochemical (electro-corrosion) technique for recess creation in LMA-filled glass micropipettes and application of the technique to fabricate DO, ORP, and pH microelectrodes.

2. Materials and methods

2.1. Electro-corrosion method and its applications

Micropipettes were made from uncleaned and untreated single barrel borosilicate glass tubes (Sutter Instrument Co., Novato, CA, # B150-86-15) having an outer diameter of 1.50 mm and an inner diameter of 0.86 mm. Micropipettes were pulled using a Sutter Instrument’s micropipette puller (Model P-30) with a heating index of 999 and pulling index of 500. The tips of the pulled micropipettes were broken so as to get an outer tip diameter of 3–10 μm. Any pipette with a tip size > 10 μm was not used. The glass micropipettes were then filled with LMA, Belmont 2451 (44.7% Bi, 22.6% Pb, 19.1% In, 8.3% Sn, and 5.3% Cd, Belmont Metal, Brooklyn, NY), to the tip as per the method described by Pang and Zhang [8]. The other end of the LMA was then melted, and an insulated copper wire with a metal connector tip was pushed in for electrical connections.

The electro-corrosion unit consisted of a 3V battery operated DC power source (custom made), a 40 ml borosil beaker filled with the electro-corrosion solution (Table 1), an alloy filled tapered glass micropipette (electrode) as the anode, and a Nichrome wire (Wire Tonic, Inc., Pine Grove, CA) as the cathode. Nichrome was selected as it is not easily corroded in the solutions used. Various acidified and non-acidified solutions of SnCl₂, CdCl₂, and ZnCl₂ were tried as the corrosion solution (Table 1). A current was passed through the cell for a definite amount of time. The microelectrode was withdrawn from the electro-corrosion unit from time to time and observed under a microscope to see the extent

<table>
<thead>
<tr>
<th>Test #</th>
<th>Electro-corrosion solution</th>
<th>Acid used</th>
<th>Recess length, μm</th>
<th>Time taken to form recess, min</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2 M SnCl₂</td>
<td>Not used</td>
<td>25a</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>2 M SnCl₂</td>
<td>2 ml, 0.5 N H₂SO₄</td>
<td>Not formedb</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>Not used</td>
<td>30 ml, 0.5 N H₂SO₄</td>
<td>Not formed</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>Not used</td>
<td>30 ml, Conc. H₂SO₄</td>
<td>Not formed</td>
<td>10</td>
</tr>
<tr>
<td>5</td>
<td>2 M CdCl₂</td>
<td>Not used</td>
<td>Not formed</td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td>2 M CdCl₂</td>
<td>2 ml, 0.5 N H₂SO₄</td>
<td>10c</td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td>1 M ZnCl₂</td>
<td>Not used</td>
<td>Not formed</td>
<td>10</td>
</tr>
<tr>
<td>8</td>
<td>1 M ZnCl₂</td>
<td>2 ml, 0.5 N H₂SO₄</td>
<td>15a</td>
<td>3</td>
</tr>
<tr>
<td>9</td>
<td>2 M ZnCl₂</td>
<td>2 ml, 0.5 N H₂SO₄</td>
<td>15a</td>
<td>3</td>
</tr>
<tr>
<td>10</td>
<td>3 M ZnCl₂</td>
<td>2 ml, 0.5 N H₂SO₄</td>
<td>15a</td>
<td>3</td>
</tr>
<tr>
<td>11</td>
<td>3 M ZnCl₂</td>
<td>5 ml, 0.5 N H₂SO₄</td>
<td>10b</td>
<td>3</td>
</tr>
</tbody>
</table>

*a* The wall of the micropipette in the recessed portion was very clean. Complete scouring of the LMA achieved.

*b* White precipitate was formed on addition of acid.

*c* The wall of the micropipette in the recessed portion was not clean.
of recess formation. When the desired recess length (e.g., 15–30 μm in the present study or longer as needed) was formed the microelectrode was removed from the system and kept immersed in distilled water for some time to remove any residual corrosion solution.

To demonstrate the application potentials of the recess creation method, three different kinds of metal and metal oxide microelectrodes were made using the micropipettes with a recess created by the method. Gold was electroplated onto the surface of the LMA on the recessed end to make DO microelectrodes [1,10]. The plating current used was 21–22 pA at 0.5–0.7 V, and the plating time varied between 15 and 20 min. For ORP microelectrodes [8], platinum was slowly deposited onto the surface of the LMA to fill the recess completely. The plating time used was 0.3–0.6 μA at 0.5–0.8 V, and the plating time varied between 15 and 20 min. For pH microelectrodes, recess was created on LMA-filled micropipettes (recess = 30 μm and tip diameter = 10 μm) and the recessed portion was filled with platinum using the plating method used for the ORP microelectrodes. The pH microelectrodes were constructed by anodic electrodeposition of iridium oxide on the platinum metal [11–13].

2.2. Measurement system and calibration of microelectrodes

Potential (mV) and current (pA) measurements were done using a chemical microsensor (Model II, Diamond General, Ann Arbor, MI) inside a Faraday cage (Technical Measuring Corporation, Peabody, MA). The measurement system was connected to a ground line separated from the building grounding.

The microelectrodes were calibrated relative to a custom-made Ag/AgCl microelectrode. The DO microelectrode was calibrated in 0.85% saline solution bubbled with gas containing either 0%, 10%, or 21% oxygen. The ORP microelectrode was calibrated as per the ASTM method [14] using quinhydrone saturated pH buffer of 4 and 7. It was also checked using quinhydrone saturated 0.05 M potassium hydrogen phthalate [8,9]. The pH microelectrode was calibrated using standard pH buffers of 4, 5, 7, 9 and 10.

3. Results and discussion

3.1. Recess formation

Various solutions were tried as the electro-corrosion solution. Initially, solutions of salts containing the metals as present in the LMA were tried (SnCl₂ and CdCl₂). Then compounds of metals belonging to the same group (in the Periodic Table) as the metals in the LMA were tried. Results so far indicate that acidic ZnCl₂ solution is the best candidate for recess creation in microelectrodes. The results obtained are presented in Table 1. Acidic CdCl₂ solution was good at creating a recess but the wall of the micropipette was not very clean; it appeared that traces of metals were still attached to the wall. SnCl₂ also showed some promise; however, it was observed that a small amount of metal still remained half protruding through the tip. The authors used a piece of anti-static wipe to remove the protruding metal; the recess was found to be very clean after that. Though the recess formed was always very clean in the case of SnCl₂, the authors preferred to use ZnCl₂ in the corrosion solution because there was no need for any finer handling (e.g., use of a wipe). It had been found that the finer the tip, the faster was the recess formation process. For tip diameters of 3–5 μm, the time for recess formation was as short as 1–3 min, which increased to 5–15 min when the tip diameter was > 5 μm. 30 ml of 1–3 M ZnCl₂ and 2 ml of 0.5 M H₂SO₄ when mixed together gave the optimal performance.

However, it should be noted that there is apparently no hard and fast rule in preparing the electro-corrosion solution. Any slightly acidic ZnCl₂ solution would work well. Higher acid concentrations were found to retard the process and also resulted in unsatisfactory corrosion of the LMA. For best results the microelectrode should be kept for 5–10 min in the corrosion solution after the electrical circuit is disconnected; this apparently removes all loose alloy (metal) particles from the recess. HCl was tried to replace H₂SO₄, and similar results as in the case of 0.5 N H₂SO₄ were obtained. The authors did not use salts of Bi and Pb in electro-corrosion, despite their presence in the LMA used, as such salts were not available with them at the time of this study. Once the desired results were achieved with ZnCl₂, it was not felt necessary to repeat the work with Bi and Pb salts. The authors used a Nichrome cathode for the electro-corrosion process; however, it is felt that any other conducting materials (such as graphite) inert to acidic solution can be used.

3.2. Applications

A representative calibration curve for DO microelectrodes fabricated using the present recess creation technique is shown in Fig. 1. The results are in conformity with those reported by others [1,10,15]. When making the recess with the old method [1,10], the present authors experienced several problems including a very low success rate. The most frustrating problem was that even after successful creation of the recess, the electroplating gold solution would not go into the recessed tip completely, and an air bubble would break the circuit. In such cases the recessed micropipettes had to be thrown away. This was one of the reasons that the
The authors started looking for an effective method as an alternative to the old method of recess creation.

ORP microelectrodes gave slopes of $\approx 59$ mV per unit pH change. A representative calibration curve for the ORP microelectrodes fabricated is shown in Fig. 2. The potential reading in quinhydrone saturated 0.05 M potassium hydrogen phthalate solution was $266.2\text{ mV}$ (at $23.8^\circ\text{C}$). The results are consistent with those reported by Pang and Zhang [8].

pH electrodes gave slightly super-Nernstian slopes of $\approx 62$ mV per unit pH change. A representative calibration curve for the pH microelectrodes fabricated is shown in Fig. 3. The results are consistent with those reported by Marzouk et al. [12] and VanHoudt and Lewandowski [7].

3.3. Significance

The old method of recess creation is more an art than a science. The present method gives some scientific control over the process. The present method makes the process much easier as regards labor and time. Also, in the old method when there is a crack or a pit in the LMA wire, it is sometimes difficult to remove it without affecting the already created recess. But in the present method any reasonable amount of force and heat can be applied to remove cracks and pits, and this can be done well before recess creation. The recess length in the LMA-filled micropipette can be manipulated as needed for a specific microelectrode by varying electro-corrosion time. The optimal time needed for a recess formation would have to be judged by the worker.

The authors applied the present recessing method in the fabrication of DO, ORP and pH microelectrodes and tested them successfully. It is expected that the present method can replace the tapered wire method (Method 1) to fabricate metal and metal–metal oxide macro- or micro-electrodes. It is hoped that once a suitable electroplating solution can be prepared, any metal or metal oxide can be deposited onto the recessed end of the LMA-filled micropipette. Therefore, less amount of precious metal (e.g., platinum, iridium or gold) would be required. In addition, the present method should make fabrication of various metal and metal oxide microelectrodes much easier. Even complicated fabrication procedure for electrodes such as chlorine [5] and N$_2$O [16] may be simplified.

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References


