Semimicro pH electrodes based on quinhydrone and related systems

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A number of pH measurement systems based on quinhydrone and related compounds have been investigated for their possible use in studies of localized conditions occurring in crevices, stress corrosion cracks, and similar situations. These systems offer the advantage of using a robust electrode of a noble metal as the pH sensitive electrode, which can be made very small. However, they do require a source of the quinhydrone in solution, and this may limit their applicability. Quinhydrone is also limited to neutral and acid solutions, which proved to be a problem in the specific case of crevice chemistry of steels in sea water. Attempts to improve the performance in alkaline solutions by additions to the quinhydrone ring were partially successful, although the compound thus formed was significantly less soluble than quinhydrone, and this gave rise to difficulties in the development of stable potentials. Practical application of the quinhydrone electrode has focused on a semimicro electrode, which can be kept in the dry state, while remaining capable of registering accurate pH values very rapidly after immersion in solution. These electrodes have been successfully used in the measurement of the pH of the solution in steel crevices in sea water, and of the solution percolating out of stress corrosion cracks in aluminium alloys.

INTRODUCTION

Since its development in the 1920s, the glass pH electrode has tended to dominate the field of electrochemical pH measurement, to the extent that few other pH sensitive electrode systems have received serious attention in recent times. As a part of a project concerned with the measurement of changes in chemical conditions in cracks and crevices in metals, a number of the less common systems have been studied. In part this was because the glass electrode was felt to be excessively fragile for this application, but it was also felt that alternative electrode systems merited further attention. One such system is that based on the quinhydrone redox reaction. This electrode was discovered by Haber and Russ1 in 1904, was later developed by Granger and Nelson,2 and has been reported as capable of very accurate pH measurement, providing certain restrictions are met. The compound referred to as quinhydrone is an equimolecular crystallization product of p-benzoquinone and its hydroquinone. When dissolved in solution the constituents create a redox equilibrium which is dependent on the activity of hydrogen ions

\[
\text{O} + 2H^+ + 2e^- \rightleftharpoons \text{OH} \quad \text{(1)}
\]

The electrode is easily prepared and the redox potential may be measured simply by means of a noble metal immersed in the solution. From the Nernst equation, the equilibrium potential of the quinhydrone redox reaction \( E_Q \) is given by

\[
E_Q = E_Q^0 + (RT/F) \ln a_{H^+} + (RT/2F) \ln (a_Q/a_{H_2Q}) \quad \text{(2)}
\]

where \( E_Q^0 \) is the standard electrode potential of the reaction, \( a \) the chemical activity of the indicated species in the solution, \( R \) the gas constant, \( T \) the absolute temperature, and \( F \) the Faraday constant. Since quinhydrone is an equimolecular crystallization product of the quinone and the hydroquinone, the concentrations are the same, and at low concentrations the activity coefficients are almost equal. Hence the final term in equation (2) is zero, and the electrode behaves as a hydrogen electrode. Any factor which causes the activities of the quinone and the hydroquinone to differ will clearly produce an error in the behaviour of the electrode. The need to add quinhydrone to the solution under examination is one of the limitations of the electrode, but it has been found that very small concentrations are required for accurate measurement, 0.00033 mol l\(^{-1}\) being reported as giving an accuracy of \( \pm 0.05 \) pH units.3

The major limitation in the use of the electrode results from the irreversible oxidation of the hydroquinone by dissolved oxygen. The rate of this reaction is tolerably low in acid solutions, but increases sharply above pH 8. For the work in question it was initially expected that acid pH values would generally be found, and this was not expected to be a serious disadvantage.

Substituted quinone/hydroquinones have also been studied by a number of workers, and may have certain advantages over quinhydrone. Tetrachloroquinone (commonly known as chloranil since it is produced from the action of chlorine on aniline) and tetrachlorohydroquinone were studied by Conant and Fieser4 in 1923, and were reported as giving a valid pH response, although the response of the electrode was at times erratic. These compounds do not form a quinhydrone, and therefore it is necessary to add the two compounds independently. While this may be less convenient, it does mean that better control can be exercised over the activity ratio, and hence the potential recorded. In particular, if both compounds are maintained at saturation, it would be expected that their activities should be fixed, and no salt errors should occur (except in the case of gross precipitate formation or reaction of one of the compounds).

A second quinone derivative, thymoquinone, is obtained by substituting alkyl groups on the ring. This has the potential advantage of extending the response of the electrode into the more alkaline region. Addition of the electron donating alkyl groups makes the hydroquinone a weaker acid, and it will therefore not ionize (and subsequently oxidize) until higher pH values.

Manuscript received 3 June 1986; in final form 14 October 1986. At the time the work was carried out, the authors were at the Corrosion and Protection Centre, UMIST, PO Box 88, Manchester M60 1QD, UK. Dr Alavi is now with Sherwin-Williams Co., Central Research Laboratory, Chicago, IL. USA.

Table 1 Calibration results for semimicro electrodes

<table>
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<tr>
<th>Treatment</th>
<th>Slope, mV/pH unit</th>
<th>Intercept, mV(SCE)</th>
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<td>(i)</td>
<td>(ii)</td>
</tr>
<tr>
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<td>56.6</td>
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Table 2 Standard deviation of measurements taken after 60 s, mV

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<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<td>1.2</td>
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<td>4.6</td>
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<tr>
<td></td>
<td>(iii)</td>
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<td>0.8</td>
<td>1.4</td>
<td>1.2</td>
<td>0.3</td>
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<td>2.6</td>
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Table 3 Standard deviation of measurements taken after 5 s, mV

<table>
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</thead>
<tbody>
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<td>2.4</td>
<td>1.5</td>
<td>1.5</td>
<td>5.1</td>
<td>4.0</td>
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<tr>
<td></td>
<td>(ii)</td>
<td>6.5</td>
<td>1.5</td>
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<td>3.3</td>
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</tr>
<tr>
<td></td>
<td>(iii)</td>
<td>2.4</td>
<td>3.9</td>
<td>3.3</td>
<td>1.6</td>
<td>2.3</td>
<td>3.3</td>
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Chloranil

On attempting to dissolve TCHQ in unbuffered sodium chloride solution, it was noted that the pH of the solution fell to ~4.5. In the buffered solutions used for calibration, some electrodes took as long as 2 h to reach equilibrium potentials, while even longer times were required in dilute, unbuffered solutions. The five platinum electrodes rarely agreed with one another, and a scatter of ~20 mV was common, even at low pH values (Fig. 2). When plotted against pH the average potential response of the electrodes in each buffer solution gave a reasonable fit to a straight line of slope 58 mV/decade up to pH 4. With increasing pH up to 7-6 the slope became shallower.

Thymoquinhydrone

No change in the pH of neutral, unbuffered 3.5% NaCl solution was detected on the addition of thymoquinhydrone. The results of the calibration measurements are shown in Fig. 3. It can be seen that the platinum wire electrodes tend to give erroneous results in the pH range 4–9, whereas the two gold electrodes give good results over the entire range. In Fig. 4 the effect of increasing the pH from 1 to 12 with a single platinum electrode is shown. In this case it can be seen that the response is linear over the entire range from 1 to 12, with an E° value of 585 mV(SCE) and a slope of 60 mV/decade at 24°C.

DISCUSSION

Quinhydrone

Once the pH semimicro electrode was dipped into the test solution it responded rapidly, giving a reasonably accurate pH measurement (within ~0.2 pH units of the correct value) after 5 s. Stable readings were attained within 10–15 s from the time of application. This proved that sufficient quinhydrone was dissolving in the electrolyte inside the electrode assembly for the platinum wire to register the appropriate potential.

Best results were obtained by cleaning the platinum wire in boiling sodium sulphite solution, and by adding the quinhydrone in the form of a fine powder rather than as a solution. These electrodes gave the most reproducible results in the long term (to within 0.05 pH units in acid solutions), and the most rapid response to the addition of solution. In general the electrodes behaved best in acid solution, and the response and accuracy tended to become poorer in solutions approaching neutrality. This was particularly evident for those electrodes (i) and (ii) in

Table 4 Difference between average potentials after 60 and 5 s, mV

<table>
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<th>pH</th>
<th>Treatment</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<tbody>
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<td>-5</td>
</tr>
<tr>
<td></td>
<td>(ii)</td>
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<td>-5</td>
<td>-3</td>
<td>-6</td>
<td>-5</td>
<td>-3</td>
<td>-3</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>(iii)</td>
<td>-3</td>
<td>-5</td>
<td>-4</td>
<td>-2</td>
<td>-3</td>
<td>-4</td>
<td>-1</td>
<td>-3</td>
</tr>
</tbody>
</table>
pH measurement over the pH range 1–10, although the low solubility renders it very susceptible to disturbance by competing reactions.

APPLICATIONS
For experiments in which quinhydrone or thymoquinhydrone can be added to the solution without fear of interfering with other redox reactions, these systems permit pH measurement with a simple platinum or gold electrode. This may be particularly suitable for research requiring pH measurements at a large number of points, since the electrodes can be constructed very cheaply and easily. Because of its susceptibility to interference, the use of thymoquinhydrone is not recommended in the absence of further research, despite its better alkaline response.

The quinhydrone semimicro pH probe offers a useful device by virtue of its rapid and accurate response to the pH of small samples of solution. In experiments on the pH of solutions in steel crevices this capability was used to study the pH of solution extracted from the crevice. The electrode appeared to work satisfactorily, although its usefulness was limited by the unexpected alkalinity of the crevice solution. It should be noted, however, that the pH range of the probe appears to extend somewhat further in this situation, since the rapidity of the measurement limits the amount of oxidation of hydroquinone which occurs. Thus it was possible to calculate the pH observed on the basis of the measured potential, and this was reasonably consistent with values obtained subsequently by other techniques.³

CONCLUSIONS
The quinhydrone electrode can be produced in a miniature form which permits rapid measurement of the pH of very small quantities of liquid. The probe needs to be reprepared for each measurement, but this is a relatively easy operation.

In systems in which the presence of quinhydrone in solution can be tolerated, the quinhydrone/platinum system offers a cheap and easy way of measuring pH values in the acid range to a high degree of accuracy.

The addition of electron attracting groups to the hydroquinone ring, as in TCHQ, increases the tendency of the molecule to oxidize, and therefore drops the upper pH limit of applicability of the system. In the case of the chloranil system this results in an unacceptable measuring range. Additionally, the low solubility of chloranil and TCHQ renders the system rather unreliable.

In contrast the addition of electron donating groups to the ring, as in thymoquinhydrone, reduces the tendency of the hydroquinone to oxidize, and thereby increases the pH range of the electrode. Unfortunately this is accompanied, at least for thymoquinhydrone, by a low solubility, which makes the system very unreproducible, although there is some indication that better results can be obtained with a gold electrode in place of the platinum.

REFERENCES

Alavi and Cottis pH electrodes based on quinhydrone system. 263