A SOLID Fe$_2$O$_3$-GRAPHITE COMPOSITE ELECTRODE FOR pH MEASUREMENT

Suchi Srivastava* and Raja Ram Pradhananga*

*Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal.

Abstract: A solid Fe$_2$O$_3$-graphite composite electrode was prepared and investigated for use as a potentiometric pH sensor. The electrode was constructed by mixing iron (III) oxide, oxidized graphite and wax that was put over silver disc onto a polypropylene rod. The response of the electrode was investigated by measuring electrode potential as a function of pH. The effect of composition of the electrode material (Fe$_2$O$_3$ and oxidized graphite ration) on the electrode response was investigated. The electrode with 40% Fe$_2$O$_3$, 30% graphite and 30% wax by mass was found to give the best potentiometric response. This electrode behaves in Nernstian manner with a potentiometric gradient of 56.6±0.4 mV per unit change in pH at 25°C within the working range of pH 2-9. The electrode was also used for the end-point detection in potentiometric acid-base titrations and found to be an excellent electrode for pH-metric titration. The effect of oxidation of electrode on pH response was investigated by dipping electrode in 0.1N KMnO$_4$, 1:1HNO$_3$ and 0.1N Ce$^{4+}$ solutions for different interval of time. This treatment of the electrode with oxidizing agents increased the standard electrode potential of the electrode however potential gradient per unit change in pH remains unaltered. Low cost, quick response and easy to prepare are the advantages of the iron oxide - graphite composite electrode as a pH sensor. However some metal ions and oxidising agents interfered in the determination of pH using this electrode which is the limitation of using these electrodes.

Keywords: Potentiometric pH sensor; Fe$_2$O$_3$-graphite composite electrode; Potentiometric titrations; pH measurement.

INTRODUCTION

The determination of pH of a solution is one of the important tasks of any analytical laboratory. The use of glass electrode, to find pH of aqueous solutions, has attained an undisputed leading position in several areas, but the glass electrode has many disadvantages, especially for untrained users. Due to the fragile nature of glass electrode coupled with high resistance and high cost, several studies have been undertaken for the development of robust electrode for pH measurement. In 1923, Uhl and Kestranek suggested for the first time the use of metal-metal oxide electrode as pH sensor. Certain metal when immersed in a solution containing dissolved oxygen, a thin film of insoluble oxide is formed over the surface of the metal which constitutes a redox pair reversible to hydrogen ion and can act as a pH probe. Carbon materials have also been widely used in electrochemistry and extensively studied as electrode materials. In addition, they are generally low cost, readily available and suitable for modification. It has been shown that various carbon materials respond to pH after activation with different activating agents. A lot of investigations were carried out during early 1970s to late 1990s on oxidizing the carbon surface and use as an electrode for pH measurement. Mc Creey in 1991 prepared carbon electrode and focused on the electrochemical pretreatment to develop a graphite oxide film on the electrode by applying a high positive potentials in acidic, neutral and basic media. However, the graphitic oxide is unstable in highly basic solution and workable and stable electrode could not be prepared. In 1995, Beilby et al. refined Mc Creey work and studied in detail the effects of potentials, pH of electrolyte and length of time of oxidation on the characteristics of the electrode. However, combination of activated carbon with other pH sensing materials like metal oxide produced a better pH sensing electrode. Graphite composite electrodes are the new category of electrodes used to measure the pH of the solution. Since early 1990s, many researchers are trying to prepare graphite composite electrode. First they focused on the graphite-quinhydrone composite electrode by mixing quinhydrone, graphite and solid paraffin. A composite electrode consisting of metal oxide, graphite and binding agent has been utilized by several authors for pH measurement. Here metal oxide is the active agent for pH response. MnO$_2$ based graphite-epoxy electrode has been used for potentiometric determination of acids and bases and this electrode exhibited a linear response in the pH range 2-13 with a slope of 53.6±0.5mV/pH at 25°C. PbO based graphite-epoxy electrode provides a linear response in the pH range from 1 to 11 with a slope of 58.7±0.3 mV/pH. A composite electrode with...
sulfated iron (III) oxide, carbon powder and epoxy resin has been constructed by Teixeira\textsuperscript{11} but this electrode is less sensitive with potential gradient of 39 mV per unit change in pH.

In the present work we report a very simple, solid Fe\textsubscript{2}O\textsubscript{3}-graphite composite electrode with paraffin wax as binder for pH measurement. The effect of amount of Fe\textsubscript{2}O\textsubscript{3} on the pH response is studied. The electrode has been successfully used in the determination of endpoint in potentiometric acid-base titrations. The effect of immersion of electrode in various oxidizing agents on pH response and effect of interfering ions on pH determination are also investigated.

MATERIALS AND METHODS

All the reagents were of analytical grade. All aqueous solutions were prepared in distilled water. The oxidative surface modification of commercial graphite powder was achieved by reflux boiling of the graphite powder with 1:1 nitric acid in a weight ratio 1:10 for 1 hour. After boiling the mixture was cooled, filtered off and the residue was rinsed with water till free from acid. The graphite so obtained was then dried at 110°C for an hour and used for the preparation of pH sensor.

Preparation composite electrode

In four different 100 mL beakers 1.0, 0.8, 0.6 and 0.4 g of oxidized graphite was taken. Then 8, 12, 16 and 20 mL of 0.6 M FeCl\textsubscript{3} solution was added respectively with continuous stirring. Then 1:1 NH\textsubscript{4}OH solution was added drop by drop under continuous stirring till precipitation of ferric hydroxide was complete. The mixture was homogenized then filtered, and washed with distilled water till washing was neutral. The residue was then dried and finally calcined at 400°C for an hour in order to obtain ferric oxide. The composite material containing different amount of ferric oxide and oxidized graphite was then mixed with 0.6 g paraffin wax. The mixture was heated in a water bath until the paraffin melted. The paste was thoroughly mixed by spatula and pressed into silver disc and mounted in polypropylene rod. The electric contact was made by the copper wire soldered to silver disc.

Instrument

All potentiometric measurements were carried out at laboratory temperature with iron oxide-graphite composite electrode and a saturated Ag/AgCl reference electrode both connected to an Osawa digital potentiometer. The electrochemical cell used for pH determination was:

\[ \text{Ag/AgCl(s), KCl(satd.)} \rightleftharpoons \text{test solution|Fe}_2\text{O}_3\text{-graphite composite electrode} \]

RESULTS AND DISCUSSION

For the preparation of composite material, the oxidized graphite is mixed with ferric chloride solution and sufficient amount of ammonium hydroxide was added. Then the brown precipitate of ferric hydroxide is obtained. The reaction involved is:

\[ \text{FeCl}_3 + 3\text{NH}_4\text{OH} \rightarrow \text{Fe(OH)}_3 + 3\text{NH}_4\text{Cl} \]

On heating, ferric hydroxide decompose to give ferric oxide.

\[ 2\text{Fe(OH)}_3 \rightarrow \text{Fe}_2\text{O}_3 + 3\text{H}_2\text{O} \]

The expected amount of ferric oxide is calculated from the above stoichiometry, is given in table 1.

<table>
<thead>
<tr>
<th>Volume of 0.6 M FeCl\textsubscript{3} (mL)</th>
<th>Amount of FeCl\textsubscript{3} (g)</th>
<th>Expected amount of Fe\textsubscript{2}O\textsubscript{3} (g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0.8132</td>
<td>0.4</td>
</tr>
<tr>
<td>12</td>
<td>1.2198</td>
<td>0.6</td>
</tr>
<tr>
<td>16</td>
<td>1.6264</td>
<td>8</td>
</tr>
<tr>
<td>20</td>
<td>2.033</td>
<td>1.0</td>
</tr>
</tbody>
</table>

The percentage composition of ferric oxide, oxidized graphite and wax in the electrode prepared in the laboratory is given in table 2.

<table>
<thead>
<tr>
<th>Name of electrode</th>
<th>% of Fe\textsubscript{2}O\textsubscript{3}</th>
<th>% of Graphite</th>
<th>% of wax</th>
</tr>
</thead>
<tbody>
<tr>
<td>IOGCE\textsubscript{20-ox}</td>
<td>20</td>
<td>50</td>
<td>30</td>
</tr>
<tr>
<td>IOGCE\textsubscript{30-ox}</td>
<td>30</td>
<td>40</td>
<td>30</td>
</tr>
<tr>
<td>IOGCE\textsubscript{40-ox}</td>
<td>40</td>
<td>30</td>
<td>30</td>
</tr>
<tr>
<td>IOGCE\textsubscript{50-ox}</td>
<td>50</td>
<td>20</td>
<td>30</td>
</tr>
</tbody>
</table>

Several parameters were investigated in order to optimize the composition of the electrode.

Effect of composition of electrode on pH response

The effect of electrode composition on the electrode response was investigated by varying the percentage of Fe\textsubscript{2}O\textsubscript{3} from 20 to 50. The plot of emf of the cell as a function of pH is shown in figure 1 for electrode with different percentage of ferric oxide. Table 3 depicts the standard electrode potential, potential gradient and correlation coefficient for the electrodes with different percentage of ferric oxide. It is evident from the plot that the electrode potential increases with increase in % of Fe\textsubscript{2}O\textsubscript{3} content in the electrode. The sensitivity of the electrode increases with increase in percentage of Fe\textsubscript{2}O\textsubscript{3} up to 40%, and then after it decreases. This may be due to the increase in activity of iron oxide on the surface of the electrode which induces the efficient charge transfer reaction at the electrode electrolyte interface. When the percentage of the iron oxide is more than 40% there is a decrease in slope of the plot. This may be attributed to increase in the electric resistance due to lower percentage of conducting graphite in the electrode. As can be seen, the best pH potential response was obtained with the electrode containing 40% Fe\textsubscript{2}O\textsubscript{3}, 30% oxidized graphite and 30% paraffin wax. The potential gradient obtained is still sub-Nerstian with a slope equal to 56.6 mV/pH and the correlation coefficient is equal to 0.998. The high correlation coefficient with potential gradient approaching to Nerstian slope means that the electrode can be used for pH measurement without much loss in sensitivity with excellent reproducibility.
Table 3: Potential gradient and standard electrode potential of composite electrode.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>% $\text{Fe}_2\text{O}_3$</th>
<th>$E^o$ (mV)</th>
<th>Slope (mV per pH)</th>
<th>$R^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>IOGCE20-ox</td>
<td>20</td>
<td>1.09</td>
<td>-32.20</td>
<td>0.985</td>
</tr>
<tr>
<td>IOGCE30-ox</td>
<td>30</td>
<td>1.24</td>
<td>-47.42</td>
<td>0.987</td>
</tr>
<tr>
<td>IOGCE40-ox</td>
<td>40</td>
<td>1.28</td>
<td>-56.58</td>
<td>0.998</td>
</tr>
<tr>
<td>IOGCE50-ox</td>
<td>50</td>
<td>1.23</td>
<td>-46.20</td>
<td>0.998</td>
</tr>
</tbody>
</table>

The potentiometric response of the $\text{Fe}_2\text{O}_3$-graphite-wax composite electrode in aqueous solutions of different pH is determined by a charge transfer reaction at the $\text{Fe}_2\text{O}_3$ / aqueous solution interface. The mechanism is a two-step process-surface hydration followed by dissociation of the surface hydroxide. The charge transfer reaction may be represented as:

$$\text{Fe}_2\text{O}_3(\text{surface}) + 3\text{H}_2\text{O} \rightarrow 2\text{Fe(OH)}_2(\text{surface})$$

$$\text{Fe(OH)}_2(\text{surface}) + \text{H}^+ \rightarrow \text{Fe(OH)}_3 + \text{H}_2\text{O}$$

The net electrode reaction responsible for pH response of the electrode may be given as:

$$\text{Fe}_2\text{O}_3(\text{surface}) + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{Fe(OH)}_2(\text{surface})$$

The electrode potential is then given by

$$E = E^o - \frac{RT}{2F} \ln \left( \frac{a_{\text{Fe(OH)}_2}}{a_{\text{Fe}_2\text{O}_3} a_{\text{H}^+}} \right)$$

$$E = E^o - 0.0591 \text{pH} \text{ at } 25^\circ \text{C}$$

**Potentiometric Titration**

The performance of $\text{Fe}_2\text{O}_3$-graphite composite electrode as an indicator electrode in potentiometric acid-base titration was evaluated by performing a series of titrations. Figure 2 shows the potentiometric curves obtained in the titration of 0.1 M HCl with 0.1 M NaOH. Figure 3 shows potentiometric curves obtained in the titration of 0.1 M phosphoric acid with 0.5 M NaOH. The plot shows clear inflation point as expected. In the titration of 0.1 M phosphoric acid with 0.5 M sodium hydroxide there are two inflation points in the curve indicating the stepwise neutralization of first and second protons of phosphoric acid.

**Interference by Different Ions**

Different metal ions and oxidising agents are likely to interfere in determination of pH by $\text{Fe}_2\text{O}_3$-graphite composite electrode. So different ions are added to a buffer solution of fixed pH and change in pH is measured after addition of interfering ions. Alkali and alkaline earth metals hardly interfere while oxidising agents such as $\text{MnO}_4^-$ and $\text{Ce}^{4+}$ induced decrease in pH. The effect of $\text{Cr}_2\text{O}_7^{2-}$ and $\text{Cu}^{++}$ ions is negligible while $\text{Fe}^{+++}$ as well as $\text{Fe}^{++}$ ions interfere in the determination of pH. Decrease in pH due to $\text{MnO}_4^-$ and $\text{Ce}^{4+}$ can be explained by the fact that both of these are strong oxidising agents and oxidizes $\text{Fe}^{++}$ ion and alters the ratio of $\text{Fe}^{++} / \text{Fe}^{+++}$ at the electrode surface that result in decrease in measured pH. So strong oxidizing/reducing agents and $\text{Fe}^{+++}$ and $\text{Fe}^{++}$ ions should not be present in the analyte solution while measuring pH by $\text{Fe}_2\text{O}_3$-graphite-wax composite electrode.

**Effect of Treating the Electrode with Oxidizing Agent**

It is observed that the emf of the cell is increased when the electrode is in contact with oxidising agent and this increase attains equilibrium value within 24 hours, after that there is hardly any change. The effect of the immersion of electrode in different oxidising agents for different times on pH responses is given in figures 4 and 5.
It is to be noted that emf of the cell is increased in all the pH range but the slope of emf vs pH curve remained constant. This means that the treatment of the electrode with oxidizing agent do not affect the sensitivity of the electrode but only altered the standard electrode potential. The increase in emf of the cell when electrode is brought into contact with oxidising agent may be due to the oxidation of Fe$^{2+}$ to Fe$^{3+}$ on the surface of the electrode where the ratio of Fe$^{2+}$/Fe$^{3+}$ decreases and emf of the cell increases which is as expected from the electrode reaction and corresponding Nernst equation.

CONCLUSION

A sensitive pH electrode can be fabricated in any chemistry laboratory from Fe$_3$O$_4$-graphite-wax composite material. The performance of the electrode depends upon the proportions of ingredients present in the composite mixture. The optimum composition of the ingredients for best performance of the electrode for pH measurement was found to be 40% of ferric oxide, 30% of oxidized graphite, and 30% paraffin wax. The electrode behaves in Nernstian manner with a slope of 56.58 mV/pH in the pH range from 2 to 9. The electrode can be used as an indicator electrode for the potentiometric titration of different acids and bases. The performance of the electrode can be used as an indicator electrode for pH measurement was found to be 40% of ferric oxide, 30% of oxidized graphite, and 30% paraffin wax. The electrode behaves in Nernstian manner with a slope of 56.58 mV/pH in the pH range from 2 to 9. The electrode can be used as an indicator electrode for the potentiometric titration of different acids and bases.

Figure 4: Plot of emf of the cell as a function of pH with original IOGCE$_{in-os}$ and IOGCE$_{ex-os}$ after treating with 0.1 N KMnO$_4$.

Figure 5: Plot of emf of the cell as a function of pH with original IOGCE$_{in-os}$ and IOGCE$_{ex-os}$ after treating with 0.1 N ammonium ceric sulphate.

be absence of oxidising agents and Fe$^{2+}$ and Fe$^{3+}$ in the test solution as these interfere in pH determination using this electrode.

ACKNOWLEDGEMENT

The authors are thankful to Central Department of Chemistry, Tribhuvan University, Kirtipur, Kathmandu, Nepal for providing available facilities for this work and one of the author (Suchi Srivastava) is also thankful to University Grants Commission, Nepal for providing M.Sc. Dissertation to carry out this work.

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