A SOLID Fe_2O_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_2O_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_2O_3 and oxidized graphite ration) on the electrode response was investigated. The electrode with 40% Fe_2O_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_2O_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[1]. 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[2]. 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[3]. 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[4] 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 *etal.*[5] 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[6-8]. A composite electrode consisting of metal oxide, graphite and binding agent has been utilized by several authors for pH measurement.[9-14] Here metal oxide is the active agent for pH response. MnO_2 based graphite-epoxy electrode[15] 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[14,16] 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[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_2O_3-graphite composite electrode with paraffin wax as binder for pH measurement. The effect of amount of Fe_2O_3 on the pH response is studied. The electrode has been successfully used in the determination of end-point 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 $FeCl_3$ solution was added respectively with continuous stirring. Then 1:1 NH_4OH 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.
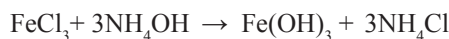
Instrument

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 Oswa digital potentiometer. The electrochemical cell used for potential measurements was:
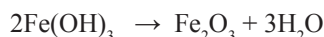
Ag|AgCl(s),KCl(satd.)|| test solution|Fe_2O_3-graphite composite electrode

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:

$FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl$

On heating, ferric hydroxide decompose to give ferric oxide.

$2Fe(OH)_3 \rightarrow Fe_2O_3 + 3H_2O$

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

Table 1: Expected amount of Fe_2O_3.

Volume of 0.6 M $FeCl_3$ (mL)	Amount of $FeCl_3$ (g)	Expected amount of Fe_2O_3 (g)
8	0.8132	0.4
12	1.2198	0.6
16	1.6264	8
20	2.033	1.0

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

Table 2: Composition of electrode.

Name of electrode	% of Fe_2O_3	% of Graphite	% of wax
$IOGCE_{20-ox}$	20	50	30
$IOGCE_{30-ox}$	30	40	30
$IOGCE_{40-ox}$	40	30	30
$IOGCE_{50-ox}$	50	20	30

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_2O_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_2O_3 content in the electrode. The sensitivity of the electrode increases with increase in percentage of Fe_2O_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_2O_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 corelation 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.
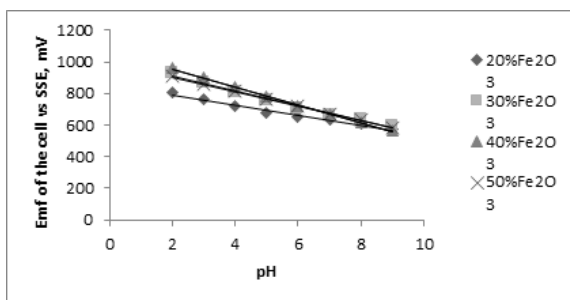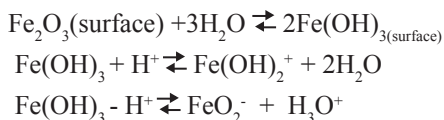
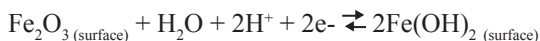Figure 1: Plot of emf against pH for Fe_2O_3-graphite composite electrode.

Table 3: Potential gradient and standard electrode potential of composite electrode.

Electrode	% Fe_2O_3	E° (mV)	Slope (mV per pH)	R^2
IOGCE$_{20-ox}$	20	1.09	-32.20	0.985
IOGCE$_{30-ox}$	30	1.24	-47.42	0.987
IOGCE$_{40-ox}$	40	1.28	-56.58	0.998
IOGCE$_{50-ox}$	50	1.23	-46.20	0.998

The potentiometric response of the Fe_2O_3-graphite-wax composite electrode in aqueous solutions of different pH is determined by a charge transfer reaction at the Fe_2O_3/ aqueous solution interface. The mechanism is a two-step process-surface hydration followed by dissociation of the surface hydroxide[11].The charge transfer reaction may be represented as:

$Fe_2O_3(surface) + 3H_2O \rightleftarrows 2Fe(OH)_{3(surface)}$

$Fe(OH)_3 + H^+ \rightleftarrows Fe(OH)_2^+ + 2H_2O$

$Fe(OH)_3 - H^+ \rightleftarrows FeO_2^- + H_3O^+$

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

$Fe_2O_{3 (surface)} + H_2O + 2H^+ + 2e^- \rightleftarrows 2Fe(OH)_{2 (surface)}$

The electrode potential is then given by

$E = E° - RT/2F \ln [a_{Fe(OH)_2}]^2/a_{Fe2O3} \cdot a_{H^+}^2$

$E = E° - 0.0591 pH$ at 25°C

Potentiometric Titration

The performance of Fe_2O_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 H_3PO_4 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.
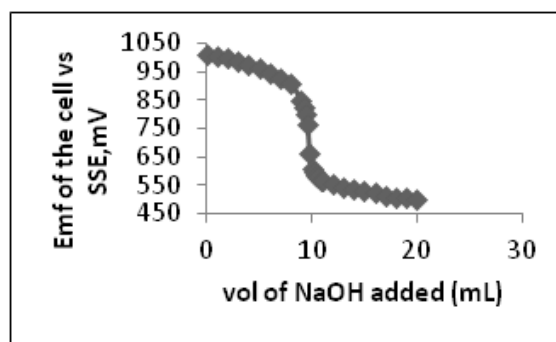

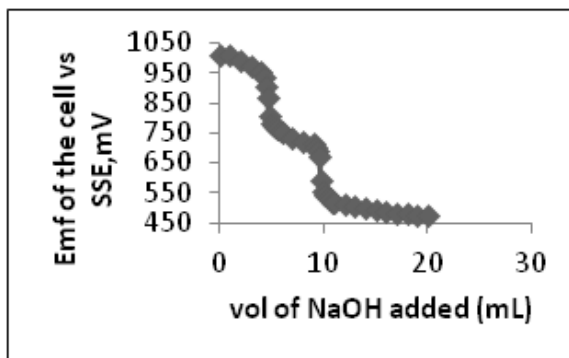Figure 2: Potentiometric titration curve of 0.1 M HCl with 0.1 M NaOH.

Figure 3: Potentiometric titration curve of 0.1 M H_3PO_4 with 0.5 M NaOH.

The experimentally determined end point matches with the theoretical end point within experimental error. This clearly indicates that Fe_2O_3-graphite composite electrode can serve as a good indicator electrode for potentiometric titration of different acids and bases.

Interference by Different Ions

Different metal ions and oxidising agents are likely to interfere in determination of pH by Fe_2O_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 MnO_4^- and Ce^{4+} induced decrease in pH.The effect of $Cr_2O_7^{2-}$ and Cu^{++} ions is negligible while Fe^{+++} as well as Fe^{++} ions interfere in the determination of pH. Decrease in pH due to MnO_4^- and Ce^{4+} can be explained by the fact that both of these are strong oxidising agents and oxidizes Fe^{++} ion and alters the ratio of Fe^{++} / Fe^{+++} at the electrode surface that result in decrease in measured pH. So strong oxidizing/reducing agents and Fe^{++} and Fe^{+++} ions should not be present in the analyte solution while measuring pH by Fe_2O_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.
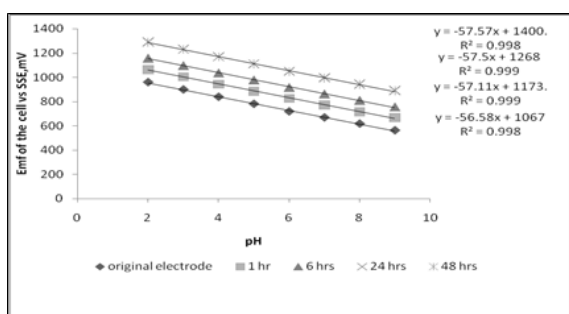
Figure 4: Plot of emf of the cell as a function of pH with original IOGCE$_{40\text{-}ox}$ and IOGCE$_{40\text{-}ox}$ after treating with 0.1 N KMnO$_4$.

Figure 5: Plot of emf of the cell as a function of pH with original IOGCE$_{40\text{-}ox}$ and IOGCE$_{40\text{-}ox}$ after treating with 0.1 N ammonium cerric sulphate .

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_2O_3-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 increase in emf of the cell is observed when the electrode is in contact with different oxidising agents but this causes no significant effect on the slope of electrode. Inexpensive, simple to use, easy to handle and non-fragility of the electrode are the advantage of this electrode over glass electrode but there should however

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

REFERENCES

1. Dussel, H., Komorsky-Lovric, S. and Scholz, F. 1995. A Solid Composite pH Sensor Based on Quinhydrone. *Electroanalysis.* **7:** 889-894.

2. Pradhananga, R.R. and Pradhananga, M. 1997. Electrochemical behaviors of electroplated and crystalline antimony electrodes. *J. Nep. Chem. Soc.* **16:** 30-34.

3. Urbanová, V., Bartoš, M., Borecká, D. and Vytřas, K. 2010. Wood-Free Resin Pencil as Low-Cost Electrode for pH Measurements. *Sensing in Electroanalysis.* **5:** 57-67.

4. McCreey, R. L. 1991. Carbon electrodes: structural effects on electron transfer kinetics. In: *Bard AJ(ed) Electroanalytical Chemistry.* **17:** 221-374.

5. Beilby, A. L., Sasaki, T. A. and Stern, H. M. 1995. *Anal Chem.* **67:** 976.

6. Scholz, F., Dussel, H. and Meyer, B.1993. A new pH sensor based on quinhydrone. *J.Electroanal Chem.* **347:** 458-459.

7. Kahlert, H., Porksen, J.R., Behnert, J. and Scholz, F. 2005. FIA acid-base titrations with a new flow through pH detector. *Anal. Bioanal. Chem.* **382:** 1981-1986.

8. Vahl, K., Kahlert, H. and Scholz, F. 2010. Rapid automatic determination of calcium and magnesium in aqueous solution by using potentiometric determination. *Electroanalysis.* **22:** 2172-2178.

9. Teixeria, M.F.S., Ramos, L. A., Cassiano, N. M., Fatibello-Filho, O. and Bocchi, N. 2000. Evaluation of a Fe_2O_3 based graphite-epoxy tubular electrode as pH electrode in flow injection Potentiometry. *J. Braz. Chem.Soc.* **11:** (1) 27-31.

10. Teixeria, M.F.S. , Ramos, L. A , Nevs, E. A. and Fatibello-Filho, O. 2000. Potentiometric determination of acids and base using a silica gel based carbon-epoxy electrode *Fresenius J. Anal Chem,* **367:** 86-89.

11. Teixeira, M.F.S., Ramos, L.A., Neves, E.A. and Cavalheiro, E.T.G. 2002. A Solid Fe_2O_3 Based Carbon-Epoxy Electrode For Potentiometric Measurements of pH *Portugaliae Electrochimica Acta.* **20:** 139-149.

12. Pásztor, K., Sekiguchi, A., Shimo, N., Kitamura, N. and Masuhara, H.1993. Iridium oxide-based microelectrochemical transistors for pH sensing. *Sens.Actuators.* **B12:** 225-230.

13. Bezdicka, P., Grygar, T., Klapste, B. and Vondrak, J. 1999. MnOx/C composites as electrode materials. I. Synthesis, XRD and cyclic voltammetric investigation. *Electrochimica Acta.* **45:** 913–920.

14. Nepal, R. and Pradhananga, R.R. 2014 Lead oxide-graphite composite electrode for pH measurement, *Nep. J. of Sc. and Tech* (in press).

15. Teixeira, M. F. S., Moraes, F. C., Fatibello-Filho, O., Ferracin, L. C., Rocha-Filho, R. C. and Bocchi, N. 1999. A novel λ-MnO$_2$-based graphite–epoxy electrode for potentiometric determination of acids and bases. *Sensors and Actuators.* **B56:** 169-174.

16. Teixeria, M.F.S, Ramos, L. A., Cavalheiro, E. T. G. and Fatibello-Filho, O. 2001. PbO2-based graphite–epoxy electrode for potentiometric determination of acids and bases in aqueous and aqueous–ethanolic media. *Fresenius J. Anal Chem.* **370:** 383-386.