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Lead Oxide-Graphite Composite Electrode for pH Measurement

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Abstract

Lead oxide-graphite composite electrode for pH measurement had been fabricated with different percentage of PbO_2 in the composite. The proportions of lead oxide affected the sensitivity of the electrode. The electrode composed of 50% lead oxide and 50% graphite gave reproducible result and behaved in Nernstian manner with a potential gradient of -58.8 ± 0.3 mV per unit change in pH. Metal ions such as iron (II), iron (III) and lead (II) interfered in the measurement of pH, while silver (I), copper (II), oxidizing agents such as dichromate and permanganate do not interfere. In absence of interfering ion, the lead oxide-graphite composite electrode could be used for the measurement of pH from 2 to 11. This electrode can also be used as an indicator electrode for acid base titrations. Low cost, quick response, easy to fabricate are some of the advantages of the lead oxide-graphite composite electrode. This electrode is also found to be sensitive to Pb^{2+} -ions and can be used as a Pb^{2+}-ion sensor up to 10^{-4}M.

Key words: composite electrode, glass electrode, interfering ions, potentiometric titrations, surface modification

Introduction

The determination pH of a solution is very important in many of chemistry, biochemistry, microbiology work and is one of the most important tasks in analytical laboratory. Among the various methods, the use of glass electrodes has been widely adopted for pH measurement due to its good sensitivity, selectivity, and stability (Galster 1991). However, glass electrodes have several disadvantages related to the intrinsic nature of the glass membrane – high impedance of the membrane, difficulty of miniaturization, mechanical fragility and chemical instability in corrosive systems. Moreover, it presents deviations of the Nernstian behavior for very high and low pH values (Lemos *et al.* 2008). Consequently, non-glass based hydrogen ion-selective electrodes are continuously investigated and such electrodes are preferred over glass electrodes owing to robustness of such electrodes.

Carbon electrodes had been used in many electrochemical works but its use as pH sensors is not very much attractive owing to the low reproducibility, narrow measurable pH range and instability of standard potential. However, the response of the electrode with concentration changes of hydrogen ions can be improved by oxidation of the carbon surface by suitable oxidant whereby quinhydrone-like surface oxides are formed and thereby improve the sensitivity of the electrode to the activity of hydrogen ion (Migdley *et al.* 1983). The change in electrode potential per unit change in pH also depends on extent of surface oxidation and nature and composition of the oxidant used for oxidation of carbon surface. Such carbon electrodes were also found to be applicable as indicator electrodes in acid-base titrations with greater potential jumps at end point compared to glass electrodes (Kahlert 2008). Another approach of producing pH sensitive carbon based electrodes is to use composite electrodes by incorporating some hydrogen sensitive material in carbon. Szepesváry and Pungor (1971) reported the use of silicone rubber based graphite electrode as indicator electrodes in acid-base titrations. Teixeira *et al.* (1999, 2000, 2001, 2002) proposed various carbon-epoxy composite electrodes modified with silica gel or different metal oxides such as PbO_2, MnO_2 or Fe_2O_3. All these electrodes behave in sub-Nernstian manner with slope ranging from 40 to 54 mV per unit change in pH.

In the present work, we investigated the possibility of using lead oxide and modified graphite as a low cost tool for pH measurement. The electrode was constructed from a mixture of PbO_2 and graphite power with solid paraffin as a binder. The effect of composition (PbO_2 and graphite) on the response and the pH dependence of the potential in aqueous media were investigated. The stability and reproducibility of the electrode in different buffer solutions were studied. The effect of different interfering ion on pH determination and possibility of using the electrode for the determination of Pb^{2+} were also investigated.

Methodology

Surface modification of graphite

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 60 min. The mixture was cooled and filtered; the residue was filtered off and rinsed with water until the rinsing water was no longer acidic. Composite electrode was prepared using this surface oxidized graphite power.

Electrode preparation

The composite active materials used in these electrodes were prepared by mixing PbO_2 (Qualigens fine chemicals), surface oxidized graphite in following mass ratio: 1) 25:75 2) 50:50 3) 75:25 with constant paraffin wax binder. The mixture was heated until the paraffin melted and thoroughly mixed, then the paste was applied over silver disc and mounted in a polypropylene rod of diameter 10 mm. The electric contact was made by the copper wire soldered to silver plate.

Equipment

All potentiometric measurements were conducted at laboratory temperature with PbO_2-graphite composite electrode and an Ag/AgCl, KCl (satd.) reference electrode. The electrochemical cell used for potential measurements was:

Ag/AgCl(s), KCl (satd.) || test solution|PbO_2-graphite composite electrode/Ag

EMF measurement was carried out using Oswa digital potentiometer under constant stirring with a Teflon coated magnetic stirrer

Results and Discussion

Effect of electrode composition

The effect of electrode composition on the response of the lead oxide-graphite composite electrode was evaluated by measuring potential at different pH. The plots of EMF of the cell as a function of pH for the electrodes of different compositions are shown in Figure 1. The corresponding slope of such plots with correlation coefficient is given in Table 1. In general, all the electrodes respond linearly with pH, however, slope of such plots are found to depend on the composition of the electrode. The slope increased with increase in percentage of PbO_2 up to 50%, after that slope decreased. The slopes given in the Table is the average of three measurements obtained from regression analysis of EMF vs. pH plot. If we look at Table 1 we will find that the sensitivity of the electrode increases with increase in percentage of PbO_2 up to 50 %, as indicated by increase in slope of the E_{cell} vs pH plot. The increase in sensitivity of the electrode with increase in PbO_2 content may be attributed to the increase in activity of PbO_2 in the composite and 50% PbO_2 is the optimum the amount. With increase in PbO_2 above 50%, the slope decreases again and this means that the sensitivity of the electrode decreases. This may be due to the decrease in efficiency of the electrode transfer reaction due to increase in resistance of the electrode. With lower percentage of conducting graphite, the conductivity of the electrode decrease thereby occurrence of some other side reaction other than the reaction responsible to hydrogen ion sensitivity may takes place.

The electrode reaction responsible for hydrogen ion sensitivity of the electrode may be represented as follow (Eftekhari 2003):

$$PbO_2\,(s) + 2H^+\,(aq) + 2e^- \rightleftharpoons PbO\,(s) + H_2O \text{ …….. } (4)$$

And corresponding equation for electrode potential is

$E = E^{\circ} - S\,P^{H}$ …………….. (5)

where E° is the standard electrode potential and S is the potential gradient per unit pH change. For an ideal electrode, the slope should be 59.1mV at 25°C. In the present investigation the slope was found to be 58.8 mV for the electrode with 50% PbO_2 and 50% graphite. This value was the average value of three measurements. The correlation coefficient was found to be 0.999. This means that the PbO_2-graphite composite electrode with 50% PbO_2 could be a very good electrode for the pH measurement.

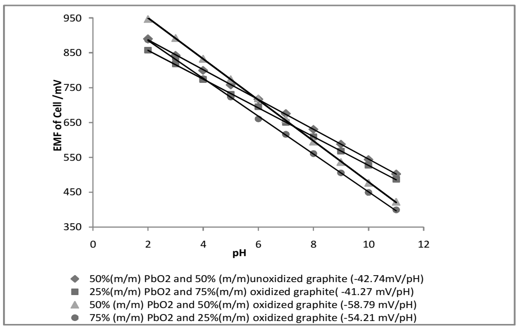

Fig. 1. P^{H} dependence of EMF of the cell of lead oxide-graphite composite electrodes with different compositions

Table 1. Response of electrode with pH **with standard deviation and correlation coefficient**

Electrode	Intercept	Slope	Correlation coefficient	Standard deviation
$E_{25\text{-ox}}$	940	-41.27	0.999	0.10
E_{50}	973	-42.47	0.999	0.48
$E_{50\text{-ox}}$	1067	-58.79	0.999	0.28
$E_{75\text{-ox}}$	994	-54.21	0.998	0.21

$E_{25\text{-ox}}$	25% lead oxide + 75 % oxidized graphite
E_{50}	50% lead oxide + 50 % unoxidized graphite
$E_{50\text{-ox}}$	50 % lead oxide + 50 % oxidized graphite
$E_{75\text{-ox}}$	75% lead oxide + 25 % oxidized graphite

Response of lead ion

The electrode is found to be sensitive to the concentration of lead ion. The electrode reaction responsible for Pb^{2+}ion sensitivity may be portrayed as follow (Lima *et al.* 2005):

$$PbO_2\,(s) + 4H^{+}\,(aq) + 2e^{-} \rightleftharpoons Pb^{2+}\,(aq) + 2H_2O \quad ………….(1)$$

At constant pH, the electrode potential of the electrode may be written as,

$$E = E^{\circ} - \frac{S}{2}\,\hat{a}\log\,[Pb^{2+}] \quad ……………….. (6)$$

Here β is the efficiency of electrode

The plot of EMF of the cell against –log $[Pb^{2+}]$ at pH 5 is shown in Fig. 2. The plot is linear one with slope equal to -57.67±0.49mV. This clearly means that the composite electrode can be used as a lead selective electrode in the concentration range of Pb^{2+} from 10^{-1} to 10^{-4} M The observed experimental data of the present investigation may be fitted to the above equation with the value of efficiency β equal to 1.95.

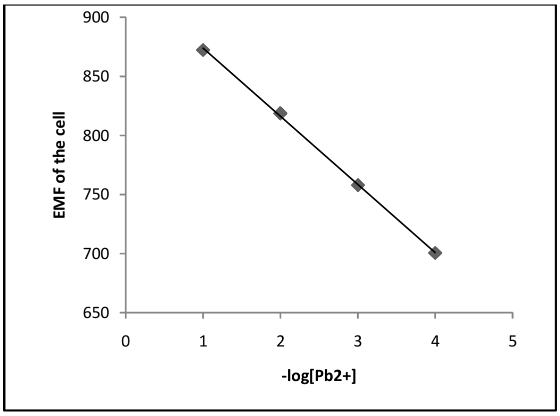

Fig. 2. Effect of lead ion concentration at constant P^{H} 5

This electrode was thus found to be sensitive to Pb^{2+} ions and could be used as a Pb^{2+} ion sensor up to 10^{-4}M concentration of lead ion at pH 5.

Potentiometric titrations

Potentiometric titration of acids and bases in aqueous media were performed by using composite electrode with 50 % PbO_2 as an indicator electrode. The electrode attained equilibrium potential within 15s. Fig. 3 presents a typical potentiometric titration curves for the titration of 10 ml 0.1M acetic acid and 0.1M hydrochloric acid with a 0.1M sodium hydroxide. In both cases clear inflexion were observed and the results were in agreement with the theoretically expected value. So, it can be concluded that lead oxide graphite composite electrode can serve as a low cost indicator electrodes for pH -metric titration. Similarly, titration of phosphoric acid with sodium hydroxide was performed. A typical titration curve is shown in Figure 4. As expected, a clear first and second inflection points were observed. Titration of a mixture of strong acid and a weak acid and titration of sodium carbonate with hydrochloric acid were also performed using lead oxide graphite composite electrode. A typical potentiometric titration curve for the titration of sodium carbonate with hydrochloric acid is shown in Fig. 5.

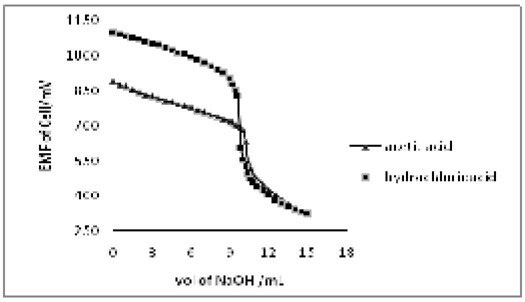

Fig. 3. Potentiometric titration curve for the titration of 10ml 0.1Ml acetic acid and 0.1M hydrochloric acid solutions separately with 0.1M sodium hydroxide solution.

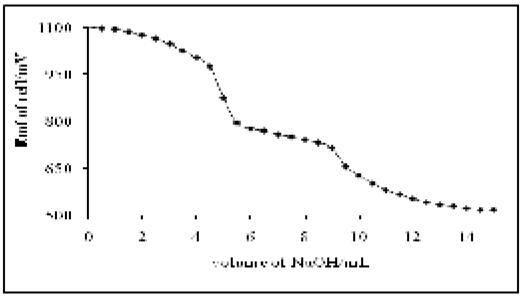

Fig. 4. Potentiometric titration curve of 0.1M phosphoric acid with 0.1N sodium hydroxide

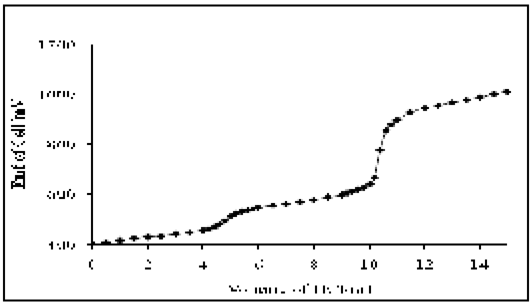

Fig. 5. Potentiometric titration curve of 0.1Nsodium carbonate with 0.1N hydrochloric acid

Effect of interference ions

The interference due to different oxidizing agent and metallic salts on the measurement of pH using lead oxide graphite composite electrode was studied. For this oxidizing agent/salt solution was added to the buffer solution till the concentration of interfering ions increased from 5×10^{-3}M to 210 $^{-2}$M and the change in p^{H} was determined. There was hardly any change in pH with the addition of $KMnO_4$, $K_2Cr_2O_7$, $AgNO_3$, and $CuSO_4$ but there was a change in P^{H} with the addition of $FeSO_4$, $Pb(NO_3)_2$ and $FeCl_3$.this is graphically shown in Fig. 6.

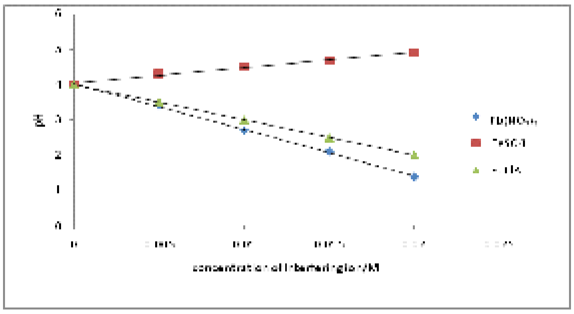

Fig. 6. Change in pH of solution with addition of interfering ion

Since the electrode is also sensitive to lead ion, it is expected that the addition of lead ion in solution interfere in the determination of pH.

A sensitivity pH sensor can be easily constructed in the laboratory from lead oxide graphite composite mixture containing equal weight of lead oxide and graphite with paraffin wax as binder. The electrode behaves in Nernstian manner with a potential gradient of 58.8±0.3 mV per unit change in pH at 25°C and can be used in pH range from 2 to 11.The electrode can be used as indicator electrode for potentiometric titration of acid with base and vice versa. Fe^{2+}, Fe^{3+} and Pb^{2+} ions interfere while oxidizing agents such as permanganate and dichromate do not interfere in the determination of pH. The electrode also responses to Pb^{2+} ion in the concentration range from 10^{-1} to 10^{-4} M. The electrode is simple to use, robust in nature, readily constructed and inexpensive. The electrode can be used for p^{H} measurement in teaching and other institute where high precision is not required.

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