

*Dedicated to prof. dr. I. C. Popescu
on the occasion of his 70th anniversary*

REPLACEMENT OF THE GLASS ELECTRODE BY GRAPHITE AT ACID-BASE POTENTIOMETRIC TITRATIONS

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ABSTRACT. Examples are shown that the paraffin-impregnated graphite (PIGE) electrode can be used as a replacement of the fragile and expensive glass electrodes in acid-base potentiometric titration. Based on the preliminary investigations this, simple, robust and cheap electrode can be an alternative of the electrodes used in the practice at present. The open-circuit potential of the paraffin-impregnated graphite in aqueous solutions of different pHs is not sensitive to the presence of oxygen. Because of the large difference between the open-circuit potential and the pH-dependent formal potential determined by using the mid-peak potential obtained by cyclic voltammetry, it can be stated that the pH dependence is due to a surface ionic exchange process with the participation of the oxidized surface groups of carbon.

Keywords: *potentiometric titration, acid-base titration, paraffin-impregnated graphite electrode*

INTRODUCTION

Glass electrodes have been used for more than a century for the measurement of pH and also in the case of acid-base titration. The story has started when Max Cremer (1865 - 1935) recognized that the potential of a glass membrane responded to the acidity of the solution [1]. Albeit hydrogen electrode and several other electrodes applied in a carefully designed cell supply exact data concerning the mean activity of hydrogen ions, glass electrode is overwhelmingly used in practice and almost exclusively at acid-base titrations. The theoretical understanding of the functioning of the glass electrode by

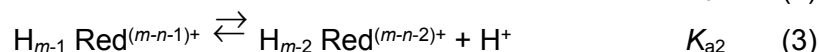
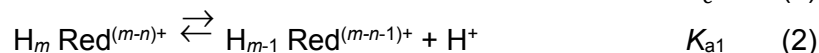
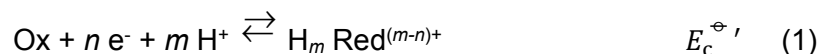
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now is well-established [2-6]. However, there are several shortcomings of the glass electrodes. A calibration is needed, they are fragile and expensive. Several electrodes have been tested, among others quinhydrone [3], metal-metal oxide electrodes [7, 8], graphite [9-12], and polymers [13, 14], which are sensitive and show an appropriate selectivity to the hydrogen ion concentration, and a fast response to the change of pH, as well as can be used more conveniently.

In fact, the working principle of a glass electrode essentially differs from the other electrodes listed above. Glass is a solid electrolyte which is applied as a membrane between two electrolyte solutions. One of the electrolytes has a constant composition, it is the so-called internal reference solution inside the usually bulb-shaped thin glass. An internal reference electrode is immersed into this electrolyte solution. In the other side of the glass there is another solution, the hydrogen ion activity of which is to be determined, and another reference electrode is immersed into this solution. The potential difference between the two terminal reference electrodes is measured. Albeit it is a classical arrangement for measuring the membrane potential, in fact, the potential difference between the glass and the contacting outer electrolyte is caused by an interfacial ionic exchange process [2-5]. Because the standard (or formal) potential is unknown, the glass electrode should be calibrated.

There are electrodes, e.g., the quinhydrone electrode, where the formal potential ($E_c^{\ominus'}$) is known with a relatively high accuracy. In these cases a redox reaction occurs where the electron transfer steps coupled with protonation:



where: K_{a1} and K_{a2} are the dissociation constants of the hydroquinone.

For $m = n = 2$, e.g., for the quinhydrone electrode the following Nernst equation can be written

$$E = E_c^{\ominus'} + \frac{RT}{nF} \ln \left(\frac{a_{\text{ox}}}{a_{\text{red}}} \frac{1 + K_{a1} a_{\text{H}^+} + a_{\text{H}^+}^2}{K_{a1} K_{a2}} \right) \quad (4)$$

In this paper we deal with the application and the working principle of the paraffin-impregnated graphite electrode (PIGE) for acid-base potentiometric titration.

RESULTS AND DISCUSSION

Electrodes based on graphite are considered as a quinhydrone-type electrode [9-12]. Usually these electrodes are activated, i.e., treated with a strong oxidant, e.g., with permanganate dissolved in sulfuric acid in order to increase the potential jump at the end-point of the acid-base potentiometric titration. However, the idea that a quinone-hydroquinone redox couple is formed on the graphite surface as a consequence of the oxidation of graphite is not entirely true. There are oxo- and probably hydroxide groups on the graphite surface without any additional oxidation, most likely due to the reaction between the oxygen from air and the carbon atoms on the surface. The activation certainly generates more oxo-groups, even the hydroxide groups that were present also being oxidized to oxo-groups. After activation the potentiometric curves starts at about 1 V when acid is titrated by a base. Without activation the starting potential under similar conditions is between ca. 0.2 and 0.8 V [10]. However, the difference in the end-potential, i.e., in basic solution is much smaller. Albeit we still have reasonable titration curves. Of course, the potential jump is smaller. Figures 1 and 2 show examples for acid-base titration, when the performance of PIGE is compared with that of a glass electrode in the course of the titration of a strong acid by a strong base (Fig. 1), and that of a weak base by a strong acid (Fig. 2).

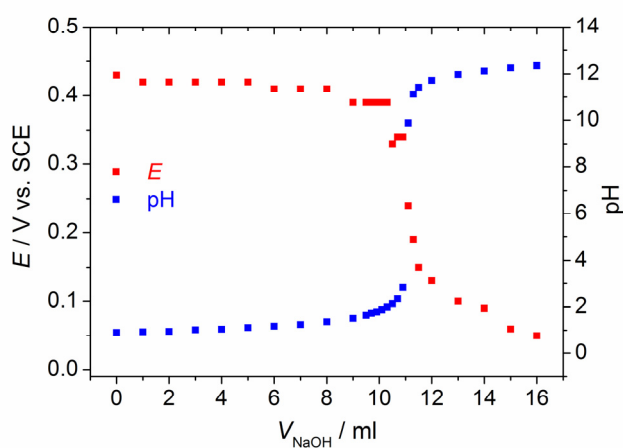


Figure 1. Potentiometric titration curves obtained for the titration of 100 cm³ of 0.1 mol dm⁻³ HClO₄ with 1 mol dm⁻³ NaOH at a PIGE (E vs. V curve) and at a glass electrode (pH vs. V curve), respectively.

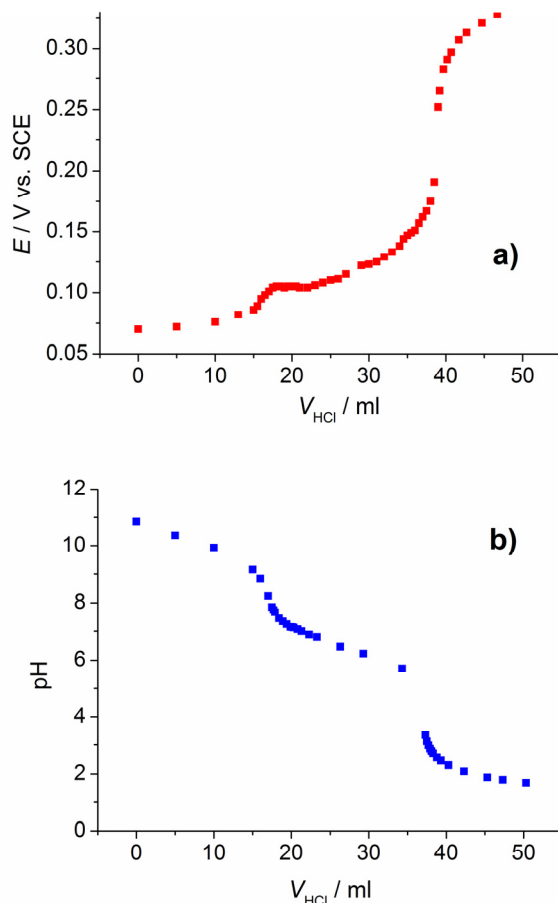


Figure 2. Potentiometric titration curves obtained for the titration of 2.5 mmol Na_2CO_3 dissolved in 100 cm^3 water by 0.1 mol dm^{-3} HCl at a PIGE (a) and a glass electrode (b), respectively.

If there is a redox couple on the surface, the formal potential of it can be determined by the help of cyclic voltammetry. The cyclic voltammetric curves obtained for a PIGE in acidic and basic media, respectively, are shown in Figures 3 and 4. It is evident from the cyclic voltammetric curves that i) there are two – more or less well-defined – pairs of peaks, ii) these peaks shift with the pH with ca. 60-65 mV/pH, iii) the formal potentials of these redox couples are ca. 0.3 V and 0 V. Therefore, if the starting potential in the case of the voltammetric curves is higher than ca. 0.6 V, there is only the oxidized form of the redox couple exists.

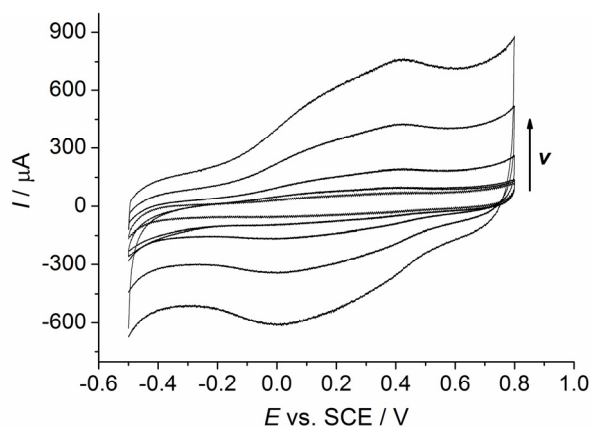


Figure 3. Cyclic voltammograms of a PIGE electrode in contact with 0.5 mol dm^{-3} H_2SO_4 solution. Scan rates are 5, 10, 20, 50, and 100 mV/s, respectively.

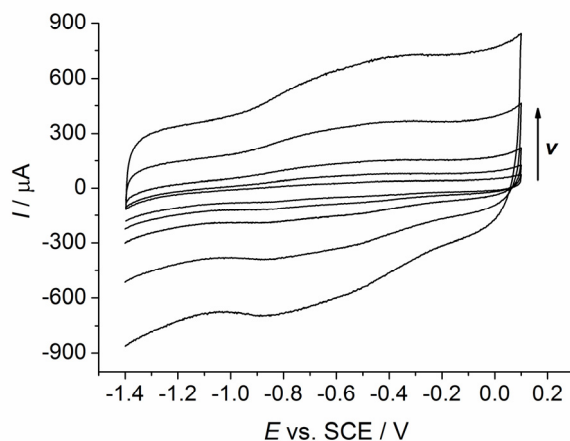


Figure 4. Cyclic voltammograms of a PIGE electrode in contact with 0.1 mol dm^{-3} NaOH solution. Scan rates are 5, 10, 20, 50, and 100 mV/s, respectively.

It follows that the simple quinone-hydroquinone concept is not adequate in the case of the so-called activated graphite electrode, and even below ca. 0.6 V the open-circuit potential in acid solution is far from the formal potential, i.e., the ox/red ratio is far from 1. Albeit in this case beside the “fully oxidized” reduced form(s) may also exist, and those may be protonated, partially

protonated or unprotonated depending on the pH of the solution. One can estimate the ratio of the oxidized and reduced forms from the formal potentials determined by the cyclic voltammetric experiments. On the other hand, at high positive potentials two possibilities can be considered. There is only the protonation of the fully oxidized groups occurs and/or further oxidation of the surface carbon atoms takes place resulting in the formation of –COOH groups. In fact, several other groups beside quinone, hydroquinone, carboxyl are assumed on the carbon surface, such as hydroxyl, keto, ether, anhydride, phenolic, lactone, epoxy bridges etc. [15]. The situation is even more complicated taking into account the different planes and sites of the graphite (edge plane, basal plane, defect sites etc.). Nevertheless, if we consider only quinone (oxo groups) or carboxyl groups as a result of the further oxidation, the potential of the electrode is determined by an ionic exchange process on the surface similarly to the glass electrode, and nothing to do with the quinone-hydroquinone redox couple. It follows that during the titration the graphite remains in its unreduced form or only slightly reduced, and we are far from the 1:1 ox/red ratio. We may assume that the open-circuit potential, $E_{ocp}^{\ominus'}$ is determined by the proton transfer at the electrode surface; i.e., the potential is related to the ratio of the activities of the protonated and unprotonated forms, which eventually leads to an equation similar to that of the glass electrode:

$$E = E_{ocp}^{\ominus'} + \frac{RT}{nF} \ln \left(\frac{a_C a_{H^+}}{a_{CH}} \right) \quad (5)$$

Assuming a constant a_C/a_{CH} ratio

$$E = E_{ocp}^{\ominus'} + \frac{RT}{nF} \ln a_{H^+} \quad (6)$$

If $n=1$ we arrive at the equation used in the case of the glass electrode

$$E = E_{ocp}^{\ominus'} - 0.059 \ln \text{pH} \quad (7)$$

Of course, the pH dependence can also be observed when the graphite is (partially) reduced, in this case the following equation is operative

$$E = E_c^{\ominus'} + \frac{RT}{F} \ln \left(\frac{a_{ox} a_{H^+}}{a_{red}} \right) \quad (8)$$

Nevertheless, the ox/red ratio is rather uncertain after an electrochemical reduction because “due the reaction with oxygen” the ox/red ratio, and consequently the open-circuit potential increases.

CONCLUSIONS

Graphite electrode especially the paraffin impregnated graphite (PIGE) rod can be used as a replacement of the fragile and expensive glass electrodes in acid-base potentiometric titration. Based on the preliminary investigations this, simple, robust and cheap electrode can be an alternative of the electrodes used in the practice at present. The open-circuit potential of the paraffin impregnated graphite in aqueous solutions of different pHs is not sensitive to the presence of oxygen. Because of the large difference between the $E_{ocp}^{\ominus'}$ and the pH-dependent formal potential ($E_c^{\ominus'}$) determined by using the mid-peak potential obtained by cyclic voltammetry, it can be concluded that the pH dependence is due to a surface ionic exchange process. It follows that the concept that has been generally accepted in the previous literature is not correct. Of course, it would be better to establish the potential at $E_c^{\ominus'}$, i.e., at the ratio $a_{ox}/a_{red} = 1$, however, at open-circuit conditions a positive drift of the potential occurs, probably due to the effect of oxygen.

EXPERIMENTAL SECTION

Spectral grade graphite rods with 5 mm diameter and 6 cm long were used. In order to decrease the background current and the contamination during successive experiments these graphite rods were impregnated by paraffin. For the preparation of PIGE, solid paraffin with low melting point was melted in a closed vessel in a water bath. The graphite rods were immersed into the paraffin and the vessel was evacuated. The impregnation was finished when no more gas bubbles evolved which took ca. 2 hours. Then ambient pressure was established, and the rods were removed before the paraffin solidified again [16]. The PIGE rods were placed onto filter paper, and allowed to cool down and dry. The lower end of the rods was carefully polished. In order to renew the surface the electrode was polished after each experiments. Analytical grade chemicals such as $HClO_4$, HCl , H_2SO_4 , (Sigma Aldrich), Na_2CO_3 , Na_2SO_4 , $NaOH$ (Molar Chemicals), KH_2PO_4 , Na_2HPO_4 , (Reanal) were used as received. Doubly distilled water was used (Millipore water). All solutions were purged with oxygen-free argon (purity: 5.0, Linde Gas Hungary Co. Ltd.), and an inert gas blanket was maintained during the cyclic voltammetric experiments. In the case of potentiometric titration with the PIGE indicator electrode argon bubbling or magnetic stirring was also used. However, when the parent (unreduced) compound was applied, there was no difference in the presence of oxygen or when the oxygen was removed. A sodium chloride saturated calomel electrode

(SCE) was used as the reference electrode which was carefully separated from the main compartment by using a double frit. A platinum wire served as the counter electrode. An Elektroflex 453 potentiostat and a Universal Frequency Counter PM6685 (Fluke) connected with an IBM personal computer were used for the control of the measurements and for the acquisition of the data. The variation of pH of the solution during the potentiometric titration was detected by a calibrated glass electrode (OP-0719P Radelkis, Budapest) by using a pH meter (Cole-Parmer, Chemcadet, Model 05986-62, U.S.A.).

ACKNOWLEDGMENTS

Financial support of the National Scientific Research Fund (OTKA K100149) is acknowledged.

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