Sensing in Electroanalysis

Vol. 5 (K. Vytřas, K. Kalcher, I. Švancara, Eds.), pp. 57-67

ISBN 978-80-7395-348-5 (printed); 978-80-7395-349-2 (on-line)

Wood-Free Resin Pencil as Low-Cost Electrode for pH Measurements

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Abstract: We report on possible use of wood-free resin pencil (WPE) as low-cost pH electrode based on WPE coated by antimony or bismuth film as the main pH sensitive material. Sensors prepared allowed to measure pH in the range of 3-10 and 10-13. The pH electrodes proposed can take advantage in strong alkaline and corrosive systems where the use of traditional glass electrode is limited. Also, they can serve as the low-cost indicator electrodes in acid-base titrations.

Keywords: pH measurements; Carbon electrode; Wood-free resin pencil; Antimony; Bismuth

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Introduction

Measurements of pH are indispensable in a wide range of control processes as well as in clinical, environmental and food industry applications. Among the various methods, the use of glass electrodes has been widely adopted due to its good sensitivity, selectivity, stability and long lifetime [1]. 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 [2]. Consequently, non-glass based hydrogen ion-selective electrodes are preferred over glass electrodes where robustness is necessary.

Carbon materials have been widely used in electrochemistry and extensively studied as electrode materials because of their good electrical conductivity, low density, low thermal expansion and low elasticity. In addition, they are generally low cost, readily available and suitable for modification [3]. It has been shown that various carbon materials respond to pH without preliminary activation. This behavior was explained with the presence of chemisorbed oxygen on the graphite surface with formation of C=O groups [4]. Properties of the carbon electrodes themselves as pH sensors are worse in the term of reproducibility, measurable range of pH and stability of standard potential compared to glass electrodes and thus, their applications in the field of pH measurements are limited. However, the response of concentration changes of hydrogen ions on the surface of carbon electrodes can be improved by suitable activation. This activation means that electrodes are pretreated by immersion in an aqueous solution of a suitable oxidant for several minutes, e.g. permanganate, to form quinhydrone-like surface oxides [5]. The slope of pH-potential graphs depended on the structure and composition of carbon used as electrode material as shown in Table 1. The slope also depend on composition of the activation solution. Without preoxidation, electrodes exhibited a slope of -30 mV per pH unit. When soaked in acidic 0.2 M permanganate solution for 1 - 3 minutes, the slope increased giving a value of -60 mV per pH unit. The electrodes activated in such way were applicable as indicator electrodes in acid-base titrations, with end point potential jumps higher than those obtained with glass electrodes [3].

Another approach of producing pH sensitive electrodes is mechanical immobilization of microparticles onto the surface of carbon electrode. The use of composite electrodes can be traced to the early 1970s when Szepesváry and Pungor reported on the use of silicon rubber-based graphite electrode as indicator electrodes in acid-base titrations [6]. Teixera et al. proposed various carbon-epoxy composite electrodes modified with silica gel [7] or different metal oxides such as PbO_2 [8], MnO_2 [9] or Fe_2O_3 [10].

Table 1. pH slopes for different carbon structure (according to [5])

Electrode material	**Slope** [mV/pH]		
	pH 0-7	**pH 7-10**	**pH 10-13**
graphite	-88,6	-42,9	-4,5
pyrolytic carbon	-77,7	-51,7	-25,1
glassy carbon	-55 to -60	-55,2	-20

Silica gel-based carbon / epoxy electrodes were used for potentiometric determinations and showed a linear dependence of the electrode potential versus pH in the range from pH 2 to 13 with a slope of -40.5 mV per pH unit [8]. PbO_2- and MnO_2-based carbon/epoxy electrodes exhibited linear responses in pH ranges from 1 to 11 and 2 to 13, respectively, with slopes of -58.7 and -53.6 mV per pH unit, respectively [8,9], Fe_2O_3-based carbon/epoxy electrodes showed a linear response over a pH range of 2-12 with a slope of -40 mV per pH unit [10].

A possibility of electrodeposition of polymer films onto the electrode surface leading to a pH-sensitive probe has been investigated in several papers. Mandler et al. [11] used benzylated polyethyleneiminequinone-modified glassy carbon electrode for voltammetric measurements of pH. The linear working range was limited to pH values smaller than 9, similarly as observed for conventional quinhydrone electrode. Blair et al. described [12] the electrodeposition of cobalt(II) porphyrin films on glassy carbon disk electrodes. Such electrodes showed linear calibration plots of potentiometric responses with slopes from -51 to -54 mV per pH unit (in a range of pH 2-12), the lifetime of electrodes was about 3 weeks.

In this work, we investigated the possibility of using wood free resin pencil with electrodeposited either bismuth or antimony film as a low-cost tool for pH measurements [13]. Bismuth/bismuth oxide and antimony/antimony oxide electrode have successfully been used for decades as metal/metal oxide pH electrodes. Especially, antimony electrode had widely been used for pH measurements before glass electrode were introduced [14,15]. It has been reported that antimony electrodes suffer a number of drawbacks that handicapped their popularity. Among these short potential linearity of the electrode (between 3 - 8 pH), trace amounts (in ppm) of copper, tin or lead interfere with the electrochemical activity of the antimony electrode and "poison" it, the electrode is temperature sensitive or the potential of an antimony electrode is sensitive to the oxygen content of the solution. On the other hand, due to its high resistance to corrosion, the Sb-based pH electrodes are particularly suited for solutions containing hydrofluoric acid in which a glass electrode normally cannot be used. Also, antimony electrodes were suggested as attractive to the soil investigation, since they offer a means for the potentiometric pH determination without additions of any active chemical or gas [16].

Also bismuth electrode found its place in pH determination. Einerhand et al. used platinum electrodes coated with bismuth as pH indicating electrodes in strong KOH solutions (pH 14 - 16). The slope was constant when the bismuth electrode had been aged via immersion in a concentrated KOH solution. The value of the potential-pH slope depended on the KOH concentration of the ageing electrolyte - a higher KOH concentration resulted in less negative value of the slope. The pH of strong alkaline solutions could be monitored with such electrodes for several hours [17].

Experimental

Chemicals

All chemicals used for the preparation of stock and standard solutions were analytical reagent grade and purchased from Lachema (Czech Republic). The buffers used in this work were obtained from *Sevapharma*® (Czech Republic). All stock and standard solutions were prepared by dilution of relevant chemicals in double distilled water.

Apparatus

All potentiometric measurements were performed using Gryf 259 ionometers (Gryf HB, Havlíčkův Brod, Czech Republic). For electroplating, a polarographic analyzer PA 3 (Laboratorní přístroje Praha, Czech Republic) equipped with a three-electrode cell configuration and consisting of WPE as the working electrode, Ag/AgCl (with saturated KCl) as the reference and platinum as counter electrode, respectively.

Scanning electron micrographs in this work were recorded by a Hitachi Tabletop Microscope TM-1000, using an accelerating voltage of 15 kV and solid state backscattered electron detector (BSE) or by a JEOL JSM-5500, using an accelerating voltage of 20 kV.

Electrodes

Wood-Free Resin Pencil Electrode (WPE). The pencil used in this work was Conté Evolution® Graphite (BIC, France). The central part of the pencil with diameter of 2.4 mm is made of graphite particles dispersed in a thermoplastic material and thus the resulting composite matrix is electrically conducting. Central conducting part is surrounded by a polymeric insulating material, the impregnation step of conducting part is not required. According to the patent the central part is made of 30 % polystyrene-methacrylate copolymer, 10 % phthalate type plasticizer, 50 % submicroscopic particles of graphite, 5 % carbon black and 5 % talc. The upper insulating part is consisting of thermoplastic (polystyrene-methacrylate copolymer and phthalate type plasticizer). The intermediate area is made of polystyrene-methacrylate copolymer [18,19]. Electrochemical properties of WPE are similar to the properties of paraffin impregnated graphite rod. Disadvantage of WPE for some applications is its quite high electric resistivity of the conducting part - it is about 5 $\Omega.cm^{-1}$. This pencil electrode was successfully applied as convenient low-cost electrode for the "voltammetry of microparticles" technique [20].

Preparation and Activation of WPE. In all cases, the electric contact of WPE was provided with an alligator clip on the top of the pencil after cutting off a part of the insulating layer. The opposite part of pencil was cut to a plain area that served as the active surface of electrode. Renovation of the active surface area of the electrode was simply done by repeated cutting of the pencil. For further measurements, the active surface of WPE was modified either by chemical modification or *in situ* plated bismuth or antimony film.

Chemical and Electrochemical Activation of WPE. Chemical activation was achieved by immersing the pencil electrode into 0.02 M $KMnO_4$ (20 ml) acidified with of 98 % H_2SO_4 (0.5 ml) for 10 minutes. Electrochemical activation was achieved by immersing the pencil electrode into distilled water (20 ml) acidified with H_2SO_4 (0.5 ml) and applying potential of +1.7 V for 10 minutes.

Preparation of WPE Coated with Antimony or Bismuth Film. Bismuth film was prepared by simultaneously depositing of Bi on the surface of pencil electrode from 0.05 M $Bi(NO_3)_3$ acidified with HCl to pH 1 and cycling between -0.36 V and -1.6 V vs. Ag/AgCl under stirring and for carefully defined period of time. Similarly, antimony film was prepared by electrodeposition from 0.05 M $SbCl_3$ acidified with HCl to pH 1 and applying potential of -0.36 V under stirring and for defined period of time. Furthermore, three minutes and current density of 22 mA/cm^2 was used for the electroplating of either bismuth or antimony onto the electroactive surface of WPE.

Results and Discussion

The WPE as a pH Sensor

First of all, it should be emphasized that electrodes prepared from pure carbon exhibit very weak response to concentration changes of hydrogen ions. On the other hand, the sensitivity to pH can be improved by suitable chemical or electrochemical activation. Such pretreatment generates functional groups like hydroxyl, carboxyl, carboxylic etc. [5] at the surface of carbon substrates.

Taking into account the construction and fabrication process of WPE, one can expect that potential of pencil electrode itself should respond to pH changes. As carbon powder is milled and heated in air, one can assume formation of above mentioned functional groups on

the surface of carbon during the fabrication process. Moreover, carbon powder in this pencil is mixed with polystyrene-methacrylate copolymer and phthalate type plasticizer containing polar functional groups. Thanks of that, WPE can be characterized as ion selective electrode with increased selectivity toward H^+ ions. Considering all these aspects, properties of WPE itself could be similar to the carbon electrode with activated surface. This consideration was confirmed experimentally. Potential of WPE depended strongly on pH, nevertheless, the reproducibility was very bad. Surface renovation (by cutting) did not contribute to improve the behaviour. Also time needed for stabilization of potential value was rather long, in agreement with experiences obtained at chemically activated carbon electrodes [5].

Neither chemical nor electrochemical activation of WPE electroactive surface brought any improvement of potential reproducibility. The effect of these operations led to even worse results when compared with nonactivated WPE. After such electrode activation, starting values of the WPE potential were higher (then the nonactivated WPE) and slowly decreased with time, being not stable even after 90 minutes. It can hardly be expected than other ways of activation could lead to an improvement of the electroanalytical characteristics of activated WPEs compared to the nonactivated electrodes.

Bismuth and Antimony Film WPE as a pH Sensor

Further investigation was focused on coating of WPE with either bismuth or antimony film. Electroplating of both bismuth and antimony film onto the different carbon substrates have been intensively studied from 2000 or 2007, respectively, as both the metals have been introduced as alternative electrode materials to mercury in voltammetric measurements [21,22]. In all cases, these films were electroplated from the salt solution of desired metal. Character and formation of the resulting films depend strongly on the electroplating conditions, above all on the type and pH of electrolytes used for electrodeposition and electric charge applied during electrodeposition.

First of all, the working conditions for bismuth and antimony electrodeposition were studied in order to obtain sufficiently homogeneous and robust deposits on conductive materials. In the first step of investigation, electrodeposition at constant potential was done, deposition potentials of -0.36 V vs. Ag/AgCl reference electrode were found suitable. An example of an electron microscopy image of bismuth deposit obtained by this approach is shown in Fig. 1A,B.

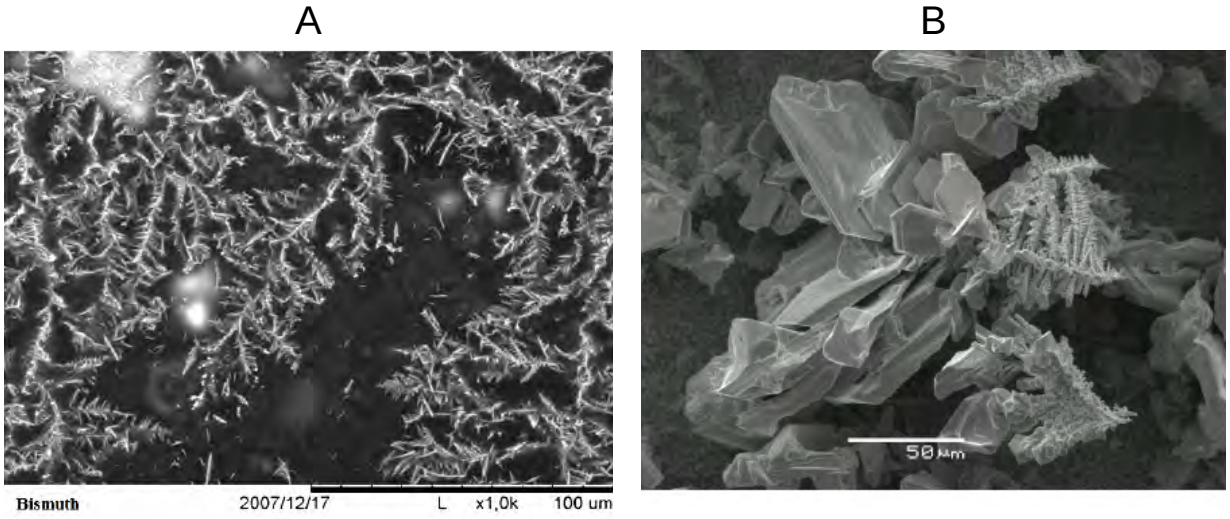

Figure 1. SEM images of bismuth film deposited from a solution containing 0,05M Bi^{3+} / HCl and applying -0.36 mV vs. Ag/AgCl.

The SEM images revealed unconsolidated bismuth coatings electrodeposited onto the electrode surface. As can also be seen from the image, the resulting bismuth film is characterized by the appearance of crystallites of a twig shape shown in detail in Figure 1B. As a consequence of this morphology, the resulting bismuth film was very fragile and could very easily be removed from the electrode surface. Because of that observation, electrodeposition of bismuth at constant current was adopted. As the result of several trials, the value of -1 mA appeared as the best for bismuth deposition. In this case, bismuth formed a homogenous and robust rhombohedral crystal lattice [23], as can be seen in Fig. 2.

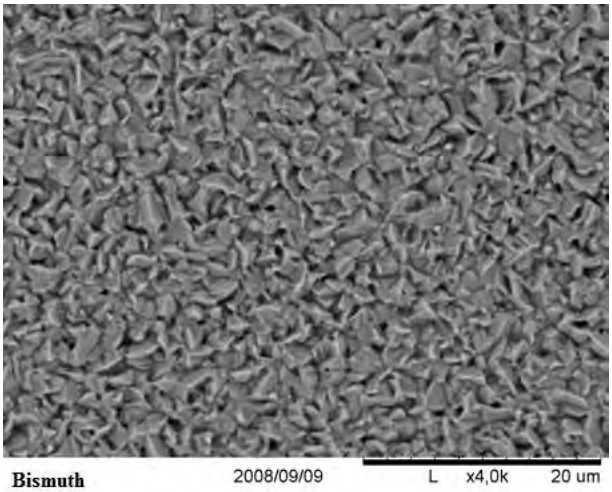

Figure 2. SEM image of bismuth film deposited from a solution with 0,05M Bi^{3+} / HCl, by applying the current -1 mA and passing a total charge of $4C/cm^2$.

Time of electrodeposition (i.e., passing of total charge) influenced thickness of the film and thus, the performance of the resulting bismuth film. At short time (less than 2 minutes), the bismuth deposit was probably not too homogeneous because the potential of the electrode was similar to that of uncoated WPE. With prolongation of the deposition time (up to 3 minutes), the film thickness and porosity grew and consequently, time need for potential equilibration increased as well. As a result of this observation, three minutes and current density of 22 mA/cm^2 were chosen as optimum for further experiments.

Similar observation was obtained for deposited antimony film. As expected, lower current densities led to smooth antimony deposits without big crystallites (Figure 3A) whereas in case of higher values (Figure 3B), the deposit was characterized by big single antimony crystals distributed randomly on the electrode surface.

WPEs obtained by above mentioned deposition (t_{dep} = 3 min, E_{dep} = -0,36 V) of either bismuth or antimony films were tested as pH sensors. The Britton-Robinson buffers (0.04 M phosphoric, boric and acetic acids) with stepwise additions of 0.2 M NaOH (pH 3 to 13) were used for measurements. Simultaneously, pH values of buffer solutions were controlled using a combined glass electrode cell, calibrated by standard buffer of conventional activity pH scale [13]. The dependences of the electrode potential on the pH for either Bi- or Sb-film WPEs were mostly linear (see Fig. 4). These dependences can be expressed by regression relationships:

E (V) = – 0.0488 pH + 0.166 (for Bi-film WPE);

E (V) = – 0.0487 pH – 0.031 (for Sb-film WPE).

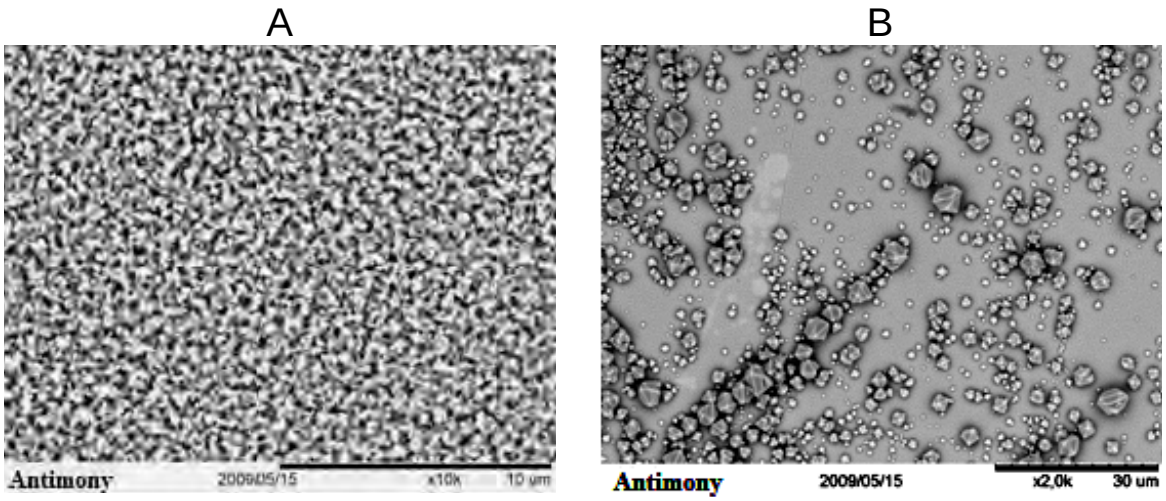

Figure 3. SEM image of antimony film deposited from a solution containing 0,05M Sb^{3+}/HCl and applying (a) -0.5mA, (b) -2.5mA.

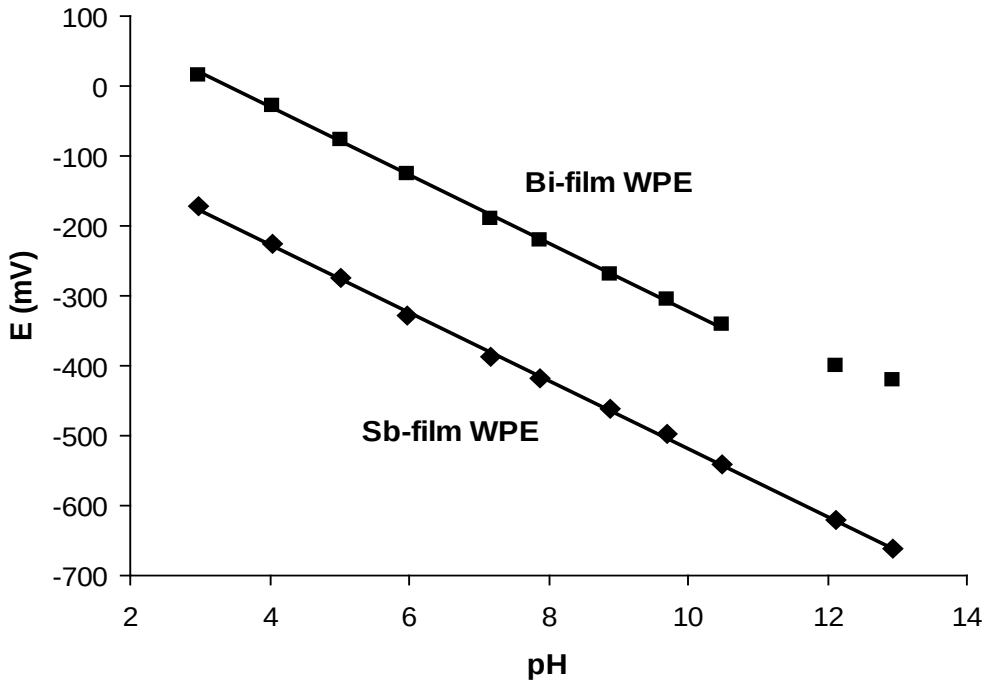

Figure 4. Potentials for both bismuth and antimony WPE as a function of solution pH using Britton-Robinson buffer solution with various pH values.

Whereas slope of the dependence obtained with Sb-film WPE was constant within the pH range studied, a decreased slope was observed in measurements with Bi-film WPE at pH > 11. It can be mentioned that similar observations were described in case of carbon paste electrodes with dispersed bismuth powder [24].

Slopes of both dependencies were practically identical, but slightly lower then Nernstian response 0.0592 V/pH. This is also in a good agreement with results other authors describing the bismuth or antimony. Such behaviour is usually interpreted as both incomplete electrode surface oxidation and interferences of disturbing ions [5,25]. Mutual distance of both dependencies was approximately 0.130 V.

Relatively good linearity of electrode potential vs. pH dependences through all pH range studied (especially for the Sb-film WPE) is marvellous. Measurements with such film electrode could be done repeatedly within one day. A long-time stability of the film was not of interest. Both electrodes were examined in various electrolyte solutions. Results of measurements were approximately the same as those obtained with glass electrode. High acidic, alkaline, reducing or oxidizing media, as well as solutions containing complex forming ligands were not tested.

Conclusions

The wood free pencil electrode with electrochemically deposited bismuth and especially antimony film is applicable to pH measurements, especially at situations preclusive of the glass electrode usage, e.g., pH measurements in acidic fluoride solutions or under conditions of possible electrode damage. While a negligible price of both Bi- and Sb-film WPEs is their main advantage, somewhat lower accuracy and a frequent film renewal can be classified as disadvantageous.

Acknowledgement

Financial grants from the Ministry of Education, Youth and Sports of the Czech Republic (projects MSM0021627502 and LC06035) are gratefully acknowledged.

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