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Development of Gold Porous Plate Electrode and Examination of Its Performance for Iodine Determination

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A novel procedure for the construction of a home-made gold porous plate electrode is described. A plate of silver and gold alloy was treated with nitric acid or alternatively by anodic oxidation to remove the silver component, leaving a porous surface having active sites for adsorption. The performance of the electrode developed was tested using iodine solution as analyte material. The parameters related to the working conditions were optimized before the examination of analytical characteristics. Under the optimal conditions, the voltammetric results show that the gold porous plate electrode offers the detection limit of 2.18 x 10^{-5} M and reproducibility of 7.8% (n = 4). The electrode performance was compared with that of glassy carbon electrode (G.C.E), gold-wire and platinized Pt electrodes in terms of current density for 2 x 10^{-4} M iodine solution. In conclusion, it is observed that the gold porous plate electrode has better current density than gold wire and platinized Pt electrodes.

Key Words: Gold porous plate electrode, determination of iodine, voltammetry.

Introduction

Voltammetry is a powerful and versatile analytical technique that offers high sensitivity, precision and accuracy as well as a wide linear range with relatively low cost instrumentation[1]. The working electrodes at which the reaction of interest occurs are generally characterized by their small surface area, which enhances polarization. In stripping techniques, micro mercury electrodes, mainly the hanging mercury drop or mercury film electrodes, are usually employed. Glassy carbon electrodes are especially good support for film electrodes.

Solid electrodes made of gold, carbon or platinum are used for the determination of metals with oxidation potentials more anodic than that of mercury. Solid noble metal electrodes are not as chemically inert as carbon. These electrodes adsorb hydrogen on their surfaces, although gold does so to a lesser degree than platinum. Hydrogen evolution commenced at a potential of –0.3 V vs. Ag/AgCl at a gold working electrode compared to –0.1 V at a Pt working electrode. Another drawback of a solid gold electrode is

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gradual passivation of the surface during repeated determinations, resulting in a decrease in sensitivity. Regeneration procedures can be simplified employing a gold film electrode rather than solid gold electrodes. For this purpose, gold is electrochemically deposited onto a substrate like poly (4-vinyl) pyridine, (PVP)[2] or the accumulation is achieved by means of an electron gun on to flexible PTFE (polytetrafluoroethylene) substrates[3].

Porous electrodes are of interest in electrocatalysis. Many types of gold porous electrodes have been developed, including gas porous electrodes, which have been shown capable of determining nanogram amounts of volatile species, and in particular of iodine[4]. The construction was usually achieved by gold deposition onto various membranes or Teflon by vapor condensation[5] or by means of a chemical reaction[6]. Thermal decomposition and amalgam surface dissolution[7] are two other ways for preparing porous gold electrodes in which Teflon is used as a support material for the attachment of the resulting electrodes[7].

The present study offers a novel approach for the preparation of a gold porous plate electrode. The main idea was to utilize the difference in dissolution characteristics of gold and silver with an oxidizing reagent, simply HNO_3, or electrochemical oxidation under suitable potential. The porous structure was obtained by chemical and electrochemical elimination of silver atoms from this alloy. Iodine was chosen as the test material for examining the performance of the constructed electrode. Silver atoms are especially suitable for the construction of the controlled pores since $r_{Agatomic}= 1.44$ and $r_{Icovalent}= 1.33$ A^0. By eliminating at least 2 silver atoms, appropriate space can be provided for iodine diffusion into the pores. Volatile iodine molecules were planned to be trapped into these pores before the voltammetric scan was applied. Since the reduction wave of iodine is at +0.3 V (vs. SCE), the use of wider anodic range solid electrodes (i.e. gold and platinum) would be beneficial for the electroanalytical detection of this substance [1]. The parameters that influence the (DC) signal for iodine molecules and the analytical characteristics of the method were investigated.

Experimental Section

Apparatus

Voltammograms were recorded using a Metrohm 693 VA Processor and 694 VA Stand. Electrolysis was carried out with a Tacussel UAPT Polarograph Tacussel PRT 500 LC Potentiostat and Tacussel GRSO Recorder. The same electrode system was used in both apparatuses, which contain a saturated calomel electrode as the reference and a Pt electrode as the auxiliary electrode.

Reagents

All reagents were of analytical grade and all the solutions were prepared with water obtained from an Ultra Pure Water System. $AgNO_3$, NaCl, CH_3COONa, KNO_3, $(NH_4)_2Fe(SO_4)_2$, $Na_2S_2O_3$, HNO_3, HCl, H_2SO_4, $HClO_4$ and iodine were all purchased from Merck, 1000 grade pure silver and gold metals were also used.

Preparation of the Gold Porous Plate Electrode

A homogenized bead of alloy was obtained by melting 0.41 g pure silver and 0.74 g of pure gold. The bead was strained homogenically and a square plate of 49.5 mm^2 was cut from this structure. The plate was attached to a gold wire by means of gold welding. Then the gold wire was coated with polyethylene powder and heated to cover the wire for insulation.

The pores were obtained by removing the silver from this plate. The elimination was achieved by immersing the plate into 1:1 diluted and then concentrated HNO_3 solution. The solution was kept at room temperature and stirred overnight.

The second elimination procedure included the electrochemical oxidation of silver by keeping the porous plate electrode at +600 mV (vs. SCE) in 0.2 M $HClO_4$ solution.

The elimination continued until all silver atoms were removed from the plate. This was checked by the observation of AgCl precipitate, which formed after the addition of NaCl to the bulk solution.

Preparation of Iodine Solution:

Iodine solution (1 x 10^{-3} M) was prepared by dissolving an appropriate amount of iodine in the required amount of water. Iodine solutions were prepared freshly before the beginning of every experiment. The concentration of the solution was also checked by titrating it with $S_2O_3^{2-}$ using the starch as the indicator.

Procedure

DC voltammograms of the porous plate electrode were recorded in the range 0-600 mV after the dearetion of 0.2 M 30 mL $HClO_4$ supporting electrolyte with N_2 gas. The electrode surface was conditioned by keeping the electrode at +600 mV for about 2 h. after each experiment. The resulting current-potential recordings were used for analytical purposes.

Results and Discussion

Following the procedure given above, the voltammograms recorded gave a DC wave signal at around +0.2 V for the reduction of iodine to iodide ions. According to the standard electrode potential values[8] and previous work[4], the reduction wave of iodine is expected at around +0.3 V (vs. SCE). This shift in the cathodic wave of iodine can be explained by the entrapment of analyte into the pores.

The type of supporting electrolyte may have an effect on the reduction wave. Among the solutions studied (KNO_3, H_2SO_4 and $HClO_4$), $HClO_4$ was chosen since a lower backgroud current was obtained with this solution (data not shown).

The effect of preelectrolysis time

The preelectrolysis time is an important parameter. One of the main disadvantages of solid electrodes is oxidation of the electrode material, which means deactivation of the active sites. For reactivation of these sites, preelectrolysis was applied to the gold porous plate electrode after the completion of each experiment. Figure 1 displays the difference at the peak currents of 2.0 x 10^{-4} M iodine after applying (a) 1 and (b) 2 h. of preelectrolysis.

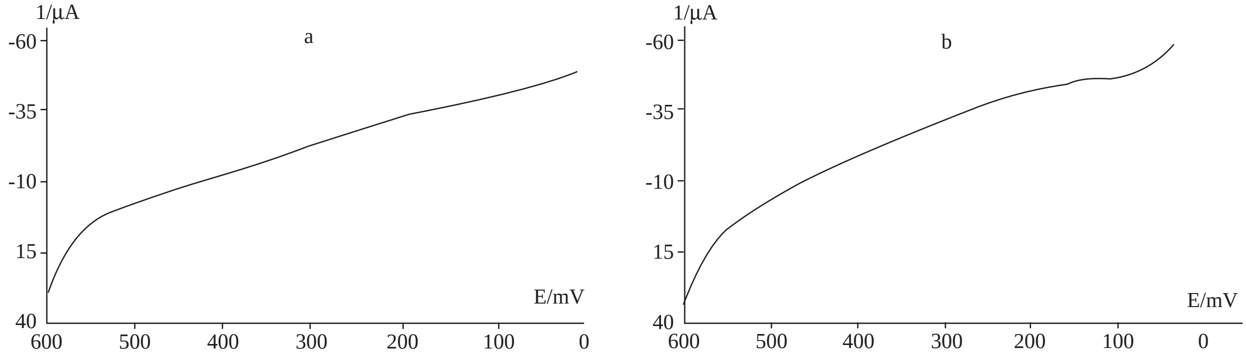

Figure 1. Voltammograms of 2.0 x 10^{-4} M iodine solution at the Au-porous plate electrode after (a) 1 h. of preelectrolysis, (b) 2 h. of preelectrolysis.

Better peak current was obtained with 2 h. because a longer preelectrolysis time increases the number of active sites and thus peak current. Since preelectrolysis longer than 2 h. would affect the practical aspect of the electrode, 2 h. was chosen as optimum time and used for further experiments.

Analytical characteristics

Under the optimal conditions mentioned above, a calibration graph was plotted as shown at Figure 2. The curve is linear between 4.8 x 10^{-5} and 2.5 x 10^{-4} M iodine solution and then it tends to stay constant due to the saturation state that is reached after the addition of 3.3 x 10^{-4} M iodine solution. For the linear range the regression coefficient was calculated as 0.998. A detection limit of 2.18 x 10^{-5} M can be estimated based on the signal to background characteristic of these data.

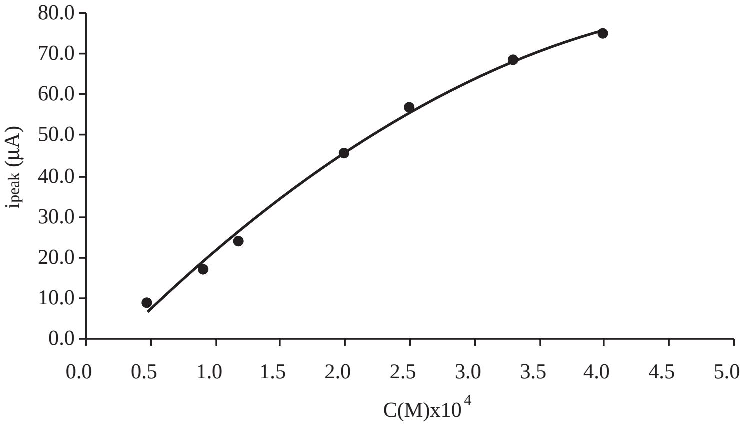

Figure 2. The calibration graph obtained under the optimal conditions with the gold porous plate electrode.

The precision was examined using 4 successive voltammetric recordings of 2 x 10^{-4} M iodine solution. Using these values, the RSD was calculated as 7.8%.

The comparison of the gold porous plate electrode with other conventional electrodes

The response of the electrode was compared with that of glassy carbon, gold wire and platinized platinum electrodes in terms of current density for 2.0 x 10^{-4} M at +0.2 V. As seen in Figure 3, the best DC wave was obtained with the gold-porous plate electrode. The current density values were: $i_{(G.C.E.)}= 0.57\ \mu A/mm^2$, $i_{(Au-wire)}= 0.13\ \mu A/mm^2$, $i_{(platinisedPt)}= 0.15\ \mu A/mm^2$, and $i_{(Auporousplate)}= 0.25\ \mu A/mm^2$. The electrode developed has better current density than platinized Pt and Au wire electrodes. This can be attributed to the adsorption capability of its pores. The pores keep the volatile substance in the electrode and provide higher current density compared to the other types of electrodes.

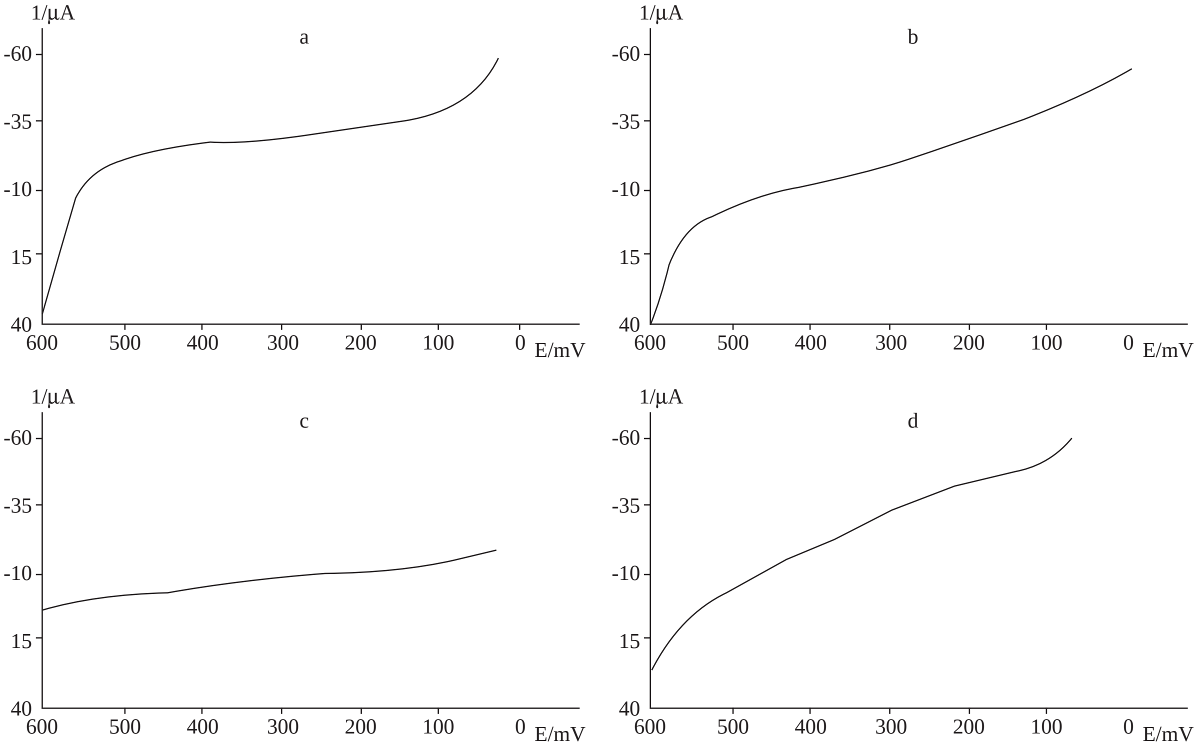

Figure 3. Voltammograms of 2.0 x 10^{-4} M iodine solution at +0.2 V with (a) platinized Pt, (b) smooth gold (c) glassy carbon, (d) gold porous plate electrodes.

Conclusion

The present study demonstrates the construction of a novel gold porous plate electrode. Iodine was used as the analyte material in order to test the performance of the electrode. The analyte was trapped in the pores with the help of adsorption from standard solutions. An almost 100 mV shift at redox potential of the iodine (+0.2 V instead of +0.3 V) confirms the adsorption phenomena. This remarkable characteristic of the electrode developed allowes its use for the detection of volatile substances.

However, the electrode has high background current, which affects the sensitivity and the attainment of lower detection limits. This may be due to the high capacitive current that results from large area of the electrode. More advanced voltammetric techniques like differential pulse (DP) and square wave (SW) can be utilized for attaining lower detection limits. On the other hand, the electrode developed may be an alternative for the determination of volatile substances by means flow injection analysis.

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