

Preparation and Characterization of a Surface Renewable Solid State Hg/HgO Reference Electrode Utilizing Gold Amalgam

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A solid state Hg(Au)/HgO reference electrode was prepared utilizing gold amalgam solid particles. Solid fine powder of the gold amalgam was prepared by chemical reduction of Au(III) with NaBH₄ followed by reduction of Hg(II) in the presence of gold fine particles. The solid content in the suspension of the gold amalgam particles and fine mercury oxide particles in DMF containing PVC was precipitated by the addition of a large amount of water to give solid Hg(Au)/HgO/PVC mixture. After drying, the mixture was pressure-molded to a physically stable Hg(Au)/HgO composite reference electrode material. The electrochemical characteristics of the electrode as a reference electrode were very similar to an ordinary Hg/HgO reference electrode. The electrode material can be molded and fabricated in any desired shape and size. The surface can be renewed by a simple polishing process whenever contaminated or deactivated. The applicability of the electrode in the electrochemical detection of carbohydrates after anion exchange separation was evaluated.

Key Words : Reference electrode, Mercury-mercury oxide, Composite electrode

Introduction

Compared to numerous recent reports on the working or indicator electrodes tailoring their electrochemical characteristics it is hard to find those reports for the reference electrodes because of their well established basic theories and easy of availability for general use. The Ag/AgCl reference electrodes have been successfully employed in various electrochemical measurements because of easy fabrication, low oxygen dependence, and small temperature hysteresis.¹⁻⁶ However in the case of the electrochemical systems containing strong alkaline media such as carbohydrate detection after anion exchange separation^{7,8} or electrochemical studies in alkaline batteries^{9,10} the malfunctions of the silver-silver chloride reference electrode are encountered frequently. The strong alkaline solution may cause electrode potential shift by undesired electrode reaction such as oxide formation. Frequent clogging or dissolution of porous junction material also causes potential drift of the system. Instead of the Ag/AgCl reference electrode the use of mercury-mercury oxide reference electrodes is favored, where the same alkaline medium can be used as an electrolyte solution in the reference electrodes. The main drawbacks of Hg/HgO reference electrode are difficulties of handling and fabricating of liquid mercury electrode materials. The bulky shape and size of the electrode and the toxicity of the mercury restrict the utility of the Hg/HgO reference electrode.

During our studies on the electrochemical detection systems in the chromatographic analysis of carbohydrate and electrochemical oxygen demand (EOD) measurements,¹¹ more reliable and suitable reference electrode system for flow cells was desired. Here, we report the preparation method of the solid-state Hg(Au)/HgO reference electrode and its electrochemical characteristics. The solid state mercury-mercury oxide electrode was prepared by utilizing

the composite electrode technique.^{12,13} The polymeric composite reference electrode matrix contains solid gold amalgam particles contacting with mercury oxide particles and PVC serves as a binder.^{14,15} The electrode can be molded in desired shapes and sizes. The surface can be renewed by a simple polishing process whenever contaminated or deactivated. The applicability of the reference electrode for the electrochemical detection of carbohydrates in ion exchange chromatographic analysis is demonstrated.

Experimentals

Reagent and instruments. All chemicals used in this work were reagent grade otherwise mentioned. Deionized water (> 18M Ω) was used for the preparation of solutions. The solutions for liquid chromatographic experiments were filtered through a 0.45 μ m membrane filters. A BAS 100W Electrochemical Analyzer from Bioanalytical System with C2 cell stand was used for cyclic voltammetric measurements. An Autolab PGSTAT Electrochemical Module from ECO CHEMIE BV was used for chronopotentiometric measurements. A pH meter from Mettler (DELTA 320) was used for potential stability tests. A LC-10Ai pump from Shimadzu was used for the chromatographic measurements. A LC-4C amperometric detector from Bioanalytical System with a Rheodyne injector having a 20 μ L loop and thin layer flow cell was used for the constant potential amperometric detection. A Carbopak PA-1 (4 \times 250 mm) anion exchange column with a Carbopak PA-guard column from Dionex was used for the separation of carbohydrate compounds. The surface morphology of the electrode was observed using an optical microscope from Olympus (BX51).

Electrode preparation. Typically 8.5 g of HAuCl₄ was dissolved in 500 mL of deionized water. Rapid addition of 500 mL of 1% sodium borohydride with vigorous stirring

turned the color of the solution from yellow to black owing to the formation of metallic gold suspension. Grayish gold amalgam suspension was formed by further addition of mercuric chloride solution (1%, 670 mL). The solution was stirred overnight to get stabilized solid state gold amalgam particles. They were filtered and dried overnight at 40 °C. The ratio between the gold and mercury was 50:50. The composition of the amalgam powder can be controlled by the amount of the mercuric chloride solution added. In a 1 L round-bottom flask, the gold amalgam particles (3.6 g) were suspended well in 25 mL of N,N'-dimethylformamide (DMF) containing 0.4 g of polyvinyl chloride (PVC) as a binder. Sudden addition of a large amount of water (ca. 500 mL) precipitated PVC along with the suspended gold amalgam. The solid content was filtered and dried overnight at 40 °C. The mercuric oxide-PVC mixture was prepared in the same way. Fine powder of 4.5 g HgO was suspended well in 25 mL of DMF with 0.5 g of PVC dissolved. Sudden addition of a large amount of water (ca. 500 mL) precipitated PVC along with the suspended HgO particles. The solid content was filtered and dried overnight at 40 °C. Both mixtures of the gold amalgam/PVC (4.0 g) and HgO/PVC (2.0 g) were mixed together and pulverized with a mortar and pestle until uniform mixture obtained. The mixture was pressure-molded into the Hg(Au)/HgO composite electrode material containing 60 wt% of 1:1 gold amalgam, 30 wt% of HgO and 10 wt% of PVC respectively. The electrode material was fabricated into desired electrode shapes. The electrical contact to the lead wire was made using silver paste. The electrodes were ground with 2000 grit SiC paper, and then polished with 0.05 μm alumina.

Results and Discussion

Physical characteristics of Hg(Au)/HgO-PVC electrode materials. The electrical resistance of the electrode having 3 mm in diameter and 5 mm in length was measured with a digital multimeter and appeared to be less than 1 Ω . Improper formation of the gold amalgam resulted in liquid mercury bleeding during the molding process. The formation of amalgam between the gold fine particles and mercury formed *in situ* from Hg^{2+} was achieved by sudden addition of Hg^{2+} solution to the suspension of gold particles containing excess sodium borohydride followed by overnight aging with vigorous stirring. The mercury oxide particles were distributed uniformly through the electrode matrix.

Electrochemical characteristics of the electrode. Cyclic voltammetry for the composite reference electrode as a working electrode was performed versus a typical homemade Hg/HgO (0.1 M NaOH) reference electrode in 0.1 M NaOH solution to characterize the electrochemical behavior. A well defined oxidation peak from Hg to HgO near 0 V was observed while the reduction of HgO to Hg was somewhat sluggish compared to the oxidation as shown in solid line in Figure 1. It has to be mentioned that the cyclic voltammograms are somewhat tilted due to the ohmic resistance of the electrode under relatively high current flow

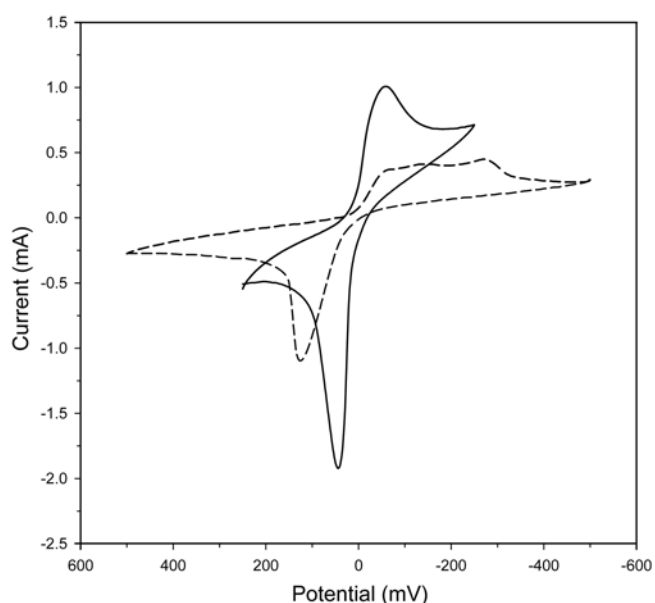


Figure 1. Cyclic voltammograms of Hg(Au)/HgO electrode in 0.1 M NaOH, scan rate 100 mV/sec, vs. Hg/HgO, NaOH (0.1 M). Dotted line: electrode prepared by using THF (contains 7.5% PVC), solid line: electrode prepared by using DMF (contains 10% PVC).

condition. The reversibility of the electrode was barely affected by the content of HgO. However the precipitation procedure of the electrode materials from their suspension was critical. At the beginning of this work tetrahydrofuran (THF) was used as a solvent for dissolving PVC and suspending solid particles. Sudden precipitation of PVC along with the gold amalgam and mercury oxide particles from THF using large amount of water resulted in large grain sized PVC particles and poor distribution of the solid particles. Consequently the electrode showed high electrical resistance about 400 Ω and poor reversibility as shown in dotted line in Figure 1. The change of HgO content did not influence significantly to the cyclic voltammetric behavior but little improvement in the reversibility. When DMF was used as a solvent, any individual grain of PVC in the solid precipitate mixture was not found, which means effective mixing of the solid content. Better electrochemical behavior of the electrode was obtained. It is thought that sudden addition of water to the suspension removes DMF from PVC more effectively compared to THF and it does not allow enough time for grain growth of PVC during precipitation.

Potential stability of Hg(Au)/HgO reference electrode was examined versus an typical homemade Hg/HgO (0.1 M NaOH) reference electrode in unstirred 0.1 M NaOH solution saturated with HgO. The electrode surface was freshly prepared and then immersed to the solution. The electrode potential was changed abruptly upon the immersion of the electrode to the solution, and then stabilized gradually as the electrode surface became equilibrated slowly with the electrolyte solution. Within an hour the electrode potential was stabilized completely as shown in Figure 2. Only a few mV of potential drift was observed during 60 hours monitoring.

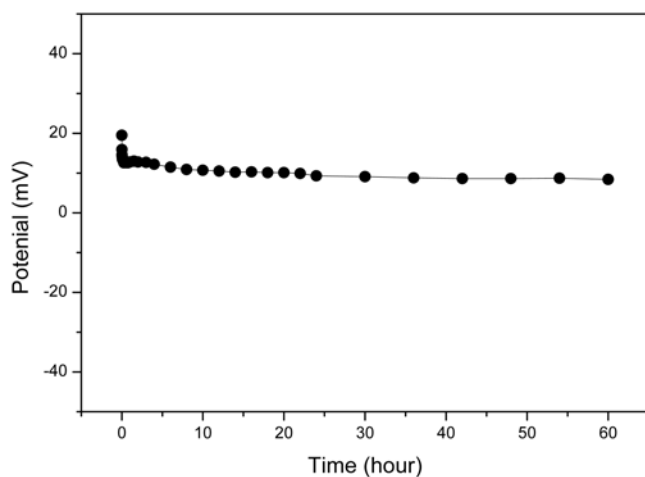


Figure 2. Potential stability test of Hg(Au)/HgO electrode in 0.1 M NaOH vs. Hg/HgO (0.1 M NaOH).

The galvanostatic behavior of the electrode was also examined. Generally to be an ideal reference electrode, the electrode potential should be resistant against current flow through the electrode. The electrode potential should be restored right after the current flow. The electrode was examined in the range of ± 0.1 – $50 \mu\text{A}$ current flow for 10 min. After applying test current in either direction, the electrode potential was monitored potentiometrically. The potential variations are shown in Figure 3. The electrode potential variations upon the galvanostatic current flows were not significant except the case of the high current experiments over $10 \mu\text{A}$. The initial electrode potential was restored immediately right after the end of galvanostatic current flows except the case of high current experiments. During the galvanostatic experiment at high current over $10 \mu\text{A}$ the potential fluctuated by the perturbation of gas evolution. In modern electrochemical measurements high current flow through the reference electrode is not expected because of the utilization of three electrode potentiometric or galvanometric electrochemical instruments and high impedance potentiometric measurement systems except unavoidable

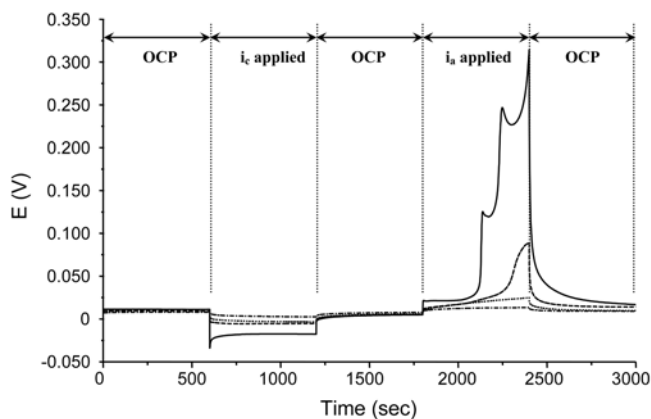


Figure 3. A typical chronopotentiogram of Hg(Au)/HgO reference electrode in the solution of sat'd HgO in 0.1 M NaOH. Applied current: $\pm 50 \mu\text{A}$ (—), $\pm 10 \mu\text{A}$ (---), $\pm 5 \mu\text{A}$ (-·-·-), and $\pm 1 \mu\text{A}$ (- - - -), OCP denotes 'open circuit potential'

cases.

1,4-Benzoquinone was selected as a probe molecule for the evaluation of the Hg(Au)/HgO composite reference electrode because of its well-known electrochemical behavior.¹⁶ Cyclic voltammetric experiments were performed using a glassy-carbon working electrode versus the Hg(Au)/HgO or Hg/HgO (0.1 M NaOH) reference electrode respectively. Only a small positive potential shift about 20 mV in the cyclic voltammogram was observed when the composite reference electrode was used (data not shown).

Applications to flow injection analysis and anion exchange chromatography. The analytical utility of the Hg(Au)/HgO composite reference electrode was examined in a flow system. The composite reference electrode was fabricated in block-type to be fit in a thin layer flow cell along with a glassy carbon working electrode. It was positioned at the down stream just next to the working electrode about 2 mm. The reference electrode was exposed directly to the mobile phase without any porous junction for internal solution. The electrodes were simply polished by an ordinary surface renewing process before use. After setting the electrode potential at $-0.150 \text{ V vs. Hg(Au)/HgO}$ reference electrode the constant amperometric response of $100 \mu\text{M}$ 1,4-benzoquinone was monitored for 100 repetitive injections (data not shown). The relative standard deviation of the amperometric responses appeared to be 1.2%, which means the reference electrode potential was kept quite constant during the repetitive injection as well as the working electrode to give reproducible data. The system was worry-free from any junction clogging or air bubble trapping in the channel. Good linear calibration characteristics for this detection system were also obtained in the range from 10^{-6} M to 10^{-3} M with the regression coefficient (R^2) of 0.998.

Figure 4 is an example showing the utility of the Hg(Au)/HgO composite reference electrode in the anion chromatographic separation of carbohydrates. The mixture of the carbohydrates were separated using an anion exchange

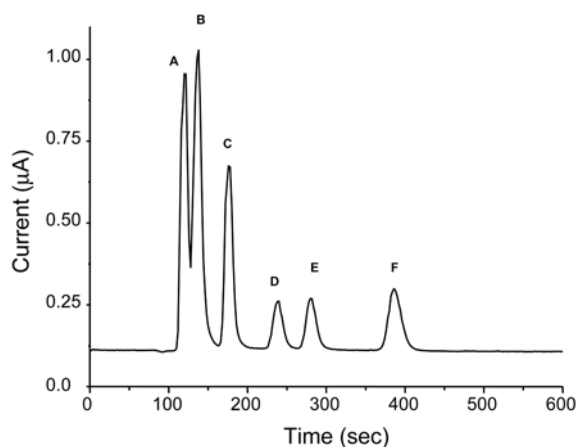


Figure 4. A chromatogram of carbohydrate mixture. A: xylitol, B: sorbitol C: glucose, D: lactose, E: sucrose, F: maltose. 1 mM each. Detected using a Cu-composite electrode vs. Hg(Au)/HgO electrode as a reference electrode at 550 mV. Caropak PA1, 4×250 mm, 0.3 M NaOH, 0.8 mL/min, $20 \mu\text{L}$ injection.

column, then detected directly using a CuO-modified composite electrode¹⁷ along with the Hg(Au)/HgO composite reference mounted on the same electrode block. Reliable electrochemical detection was possible without noticeable background signal fluctuation owing to the instability of the electrode potential.

In conclusion a novel solid-state Hg(Au)/HgO reference electrode utilizing a polymeric composite electrode technique was developed. The electrode showed similar electrochemical characteristics to the ordinary Hg/HgO reference electrode. The electrode potential was stable for a prolonged experimental period. The electrode restores the original electrode potential quickly upon the perturbation by appreciable current flow. It is much easier to handle and fabricate to any shapes and sizes. Especially in the alkaline flow system the physical configuration can be simplified by removing the porous junction. In addition the electrode surface can be renewed easily whenever contaminated or deactivated. The utility of the reference electrode in various alkaline flow systems will be examined further in our laboratory.

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