



Surface renewable nano-iridium oxide polymeric composite pH electrodes



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ARTICLE INFO

Article history:

Received 9 May 2014

Received in revised form 16 July 2014

Accepted 23 July 2014

Available online 1 August 2014

Keywords:

pH electrode

Iridium oxide

Composite electrode

ABSTRACT

A simple but effective preparation method of a surface renewable nano-iridium oxide polymeric composite electrode showing highly improved pH response characteristics was developed. Nano-iridium oxide was incorporated in polymethylmethacrylate (PMMA) matrix as an electrical conductor and active sensing material for hydrogen ion. It was prepared by the hydrolysis of $(\text{NH}_4)_2\text{IrCl}_6$ and were then simply dispersed in acetone containing PMMA. The suspension of the nano-iridium oxide and PMMA was precipitated rapidly into water and then pressure-molded to disk-type nano-iridium oxide composite electrode material. The electrode showed excellent linear response between pH 3 and 11 with a slope of -59.6 mV/pH ($R = 0.9999$) and fast response time of $\tau_{90} < 2 \text{ s}$. Steady response with an average slope of $-58.9 \pm 0.3 \text{ mV/pH}$ and $E^{\circ'}$ intercept of $653.4 \pm 2.9 \text{ mV vs. } 3 \text{ M Ag/AgCl}$ reference electrode was observed for a month without appreciable deactivation. Less porous and hydrophobic surface of the polymeric composite electrode minimized equilibration time resulting in the fast response. The electrode can be stored in deionized water or in air after uses. The lifetime of the electrode was extended greatly because the surface can be renewed reproducibly by simple polishing whenever contaminated or deactivated.

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1. Introduction

Despite the distinctive performance of the glass membrane-based pH electrode, it has drawbacks of fragility, difficulties in maintenance, and easy fouling in harsh environmental measurements. The polymeric membrane-based hydrogen ion-selective electrodes are not fragile but can tear easily. In order to improve the ruggedness of the pH electrodes, metal oxides such as TiO_2 , RuO_2 , RhO_2 , SnO_2 , Ta_2O_5 , OsO_2 , PtO_2 , or IrO_2 have been used as hydrogen ion sensing materials [1–21]. Among these oxides, iridium oxide has been used widely because of its excellent response to the hydrogen ion concentration. The electrodes have been prepared by thermal decomposition, sputtering or electrochemical deposition in the form of oxide films on the surface of their mother metals or conducting inert metals. They are mostly inert and rugged in harsh applications, and easy to be miniaturized. However, serious drift of the electrode potential due to the pores or cracks formed during decomposition and the lack of surface uniformity of the oxide films have been major drawbacks [1,9,13,20]. Such problems were overcome by a thick film IrO_2 -based pH electrode formed on the iridium wire by high temperature carbonate-melt

oxidation technique [13]. Excellent pH response characteristics and a durability of 2.5 years were achieved. Such improved characteristics have been attributed to the uniform and dense iridium oxide film on the iridium wire. Nevertheless, surface renewable pH electrodes are still desired for harsh environmental applications such as food processing, soil analysis, sludge analysis, or on-line monitoring systems where antifouling and deactivation of the sensing elements are critical.

Recently we have reported two types of surface renewable iridium oxide-based composite pH electrodes. The electrode matrix was either a polymeric carbon composite or a glass composite [20,21]. Both electrodes contain micro-fine IrO_2 particles throughout the electrode matrix. Therefore, the active surface could be regenerated reproducibly (0.7% in relative standard deviation, RSD) by simple grinding with 2000 grit SiC emery paper whenever it was deactivated or fouled. The electrodes could be stored in deionized water or even in air. The IrO_2 -modified carbon polymeric composite pH electrodes showed about -55.7 mV/pH response with fast response time ($\tau_{90} = 2 \text{ s}$), while the IrO_2 -glass composite electrode showed -58.6 mV/pH but slower response time ($\tau_{90} = 7 \text{ s}$). The carbon black in the polymeric composite electrode matrix was added as an electrical conductor to support the electrical conductivity of the electrode. The exposure of the carbon black to the test solution could not be ignored. Any substantial existence of electroactive species might generate a potential and would affect

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the measured electrode potential. We have found that the electrical conduction by the iridium oxide itself was enough for the potentiometric pH measurements through the IrO₂-glass composite electrode work. A better pH response close to the theoretical value (−59.2 mV/pH) was obtained in the glass-based IrO₂ composite electrode work by omitting the carbon black. However, the response time characteristics became worse because of the porosity of the IrO₂-glass composite electrode prepared by high temperature sintering at ambient pressure. More time was required for the surface equilibration until the electrode response stabilized. Large drift of the electrode potential was also observed in prolonged measurements. From the results of both of our previous reports [20,21] and the thick film IrO₂ electrode [13] we have reached the conclusion that the porosity or defects on the electrode surface have a critical effect on the potentiometric equilibration. Further, the pH measurement based on the redox reaction of Ir(III)/Ir(IV) couple can be performed without the aid of another conductor such as carbon black or metals.

Since the uniformity of the surface with less porosity is a critical requirement for fast potentiometric equilibration resulting in a stabilized response in a short time, we selected polymeric matrix for the compactness of the electrode matrix and nano-iridium oxide particles for better dispersion of the sensing material. Random dispersion of the nano-iridium oxide particles in the polymer solution ensured better performance of the nano-IrO₂ polymeric composite pH electrodes with very short response time and excellent response slope close to the theoretical value of −59.2 mV/pH. The polymeric composite electrode material can be pressure-molded easily at moderate temperatures in various sizes and shapes according to system requirements. The electrode is surface renewable, allowing extended lifetime, and can be stored in air conveniently without losing its activity. Here, we report the preparation method and characteristics of the nano-IrO₂ polymeric composite pH electrodes.

2. Materials and methods

2.1. Reagents and instruments

All chemicals were reagent grade and used as received unless otherwise mentioned. Ammonium hexachloroiridate(IV) was obtained from Alfa Aesar. Polymethylmethacrylate (PMMA, MW 120,000) was from Sigma-Aldrich. Aqueous solutions were prepared with deionized water (18 MΩ). In most cases, commercial pH buffer solutions (pH 4, 7, and 10) were used for the calibration of the pH meter. For stepwise pH measurement, the pH of 0.01 M H₃PO₄-H₃BO₃-CH₃COOH-KCl universal buffer solution was adjusted appropriately by adding 0.1 M NaOH or 0.1 M HCl. A combination pH glass membrane electrode (Accumet 13-670-287) with an Accumet 50 pH meter (Fisher Scientific) was used for pH monitoring. Electrode potential was measured vs. Ag/AgCl reference electrode (3 M KCl) at 25 °C. The iridium oxide content in the composite electrode material was analyzed using a thermal gravimetric analyzer (TGA 7, Perkin Elmer) at 600 °C under air atmosphere. A transmission electron microscope (TEM, Tecnai G2 20 s from FEI) was used for particle size observation of the iridium oxide nanoparticles.

2.2. Electrode preparation

Nano-iridium oxide (possibly IrO₂·xH₂O) was prepared by the hydrolysis of hexachloroiridate at elevated temperature [22]. Typically 0.40 g of (NH₄)₂IrCl₆ was dissolved in 120 mL of deionized water. The pH of the resulting reddish brown solution was adjusted to about 8.2 with 0.25 M NaOH. This was followed by heating to

95 °C with constant stirring for 1 h under reflux setting in an oil bath. The solution turned into a deep blue suspension. It was cooled down to room temperature, and then, the pH was adjusted again to pH 8.2 with NaOH solution. The process of pH adjustment and heating was repeated until the pH stabilized to near pH 8.2 for the completion of the reaction. The nano-iridium oxide was collected and washed with deionized water thoroughly using a centrifuge. The washing solvent was changed to acetone finally. After dispersing the nano-iridium oxide particles in 7 mL acetone thoroughly 0.21 g of PMMA powder for 37 wt% IrO₂ electrode was added and dissolved completely. The syrupy mixture was injected into a large amount of deionized water using a syringe with vigorous to extract the acetone out of the nano-IrO₂/PMMA mixture. After washing the solid composite mixture of nano-IrO₂/PMMA thoroughly with deionized water it was dried at 60 °C overnight and was then ground well using a ceramic mortar and pestle. The mixtures were analyzed using the TGA under air stream at 600 °C to estimate the actual iridium oxide contents in the composite materials. Because of the loss in the synthesis and mixture preparation ~10% of discrepancy in iridium oxide contents between the calculated and analyzed values was found. The analyzed iridium oxide contents are reported in this work. The mixture was pressure molded at 8 ton/cm² and 150 °C into nano-IrO₂ polymeric composite electrode materials (3 mm in length, 4 mm in diameter). They were fabricated into rod-type electrodes in a plastic housing with silver epoxy connection to copper lead wire. The surface of the electrode was ground using 2000 grit SiC emery paper and then polished using 0.5 μm alumina. The electrodes were soaked in deionized water for a day prior to use. The electrodes were stored in deionized water between daily tests.

3. Results and discussion

3.1. General characteristics of the electrodes

The surface of the polished composite electrode was smooth and shiny with less defects compared to that of the IrO₂/glass composite electrodes or IrO₂/C-black polymeric composite electrodes as shown in Fig. 1A [20,21]. The electrical resistance was higher than 40 MΩ, so it was not possible to measure it with an ordinary digital multimeter. Random noise was observed on the raw potential signals sampled in every second due to the high resistance of the composite electrode material. Therefore, ten consecutive signals were averaged manually for the estimation of the electrode potentials and response slopes in this work. Such noise can be reduced if an instrument is used having data averaging function with higher sampling rate. Nevertheless, they showed potentiometric response depending on the hydrogen ion concentration if the iridium oxide content was between 30 and 40 wt%. Sometimes surface defects (Fig. 1B) were found on the electrodes, which showed low response slope or delayed stabilization of the potential. The defects were mainly due to the micro-lumps of the iridium oxide aggregates formed by incomplete dispersion in the mixture. Since a minimum equilibration layer on the defect-free electrode surface with random distribution of the iridium oxide nanoparticles was desired for quick equilibration to enable a fast and stable electrode response, we had deep concerns on the particle size distribution and dispersion of the nano-iridium oxide particles in the polymeric matrix. TEM image of the iridium oxide nanoparticles prepared in this work is shown in Fig. 1C. The nanoparticles were about 2 nm and quite uniform in size. Rapid injection of the syrupy suspension of the nano-IrO₂/PMMA mixture in acetone to water was effective to solidify the mixture without losing good dispersion of the iridium oxide in the PMMA matrix. This composite mixture was analyzed using TGA for fine-tuning the iridium oxide content to get optimum response characteristics discussed below. High pressure

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