Surface Renewable Hydrogen Ion-Selective Polymeric Composite Electrode Containing Iridium Oxide

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A surface renewable pH electrode was prepared by utilizing composite electrode technique. Iridium oxide micro-fine particles was prepared by hydrolysis of $(NH_4)_2IrCl_6$ at elevated temperature. The iridium oxide particles were mixed with well-dispersed carbon black and then filtered. The mixture was suspended in DMF containing PVC as a binder. The mixture was precipitated rapidly by adding large amount of water. The precipitate was ground and pressure-molded to iridium oxide composite electrode material. The electrode showed linear response between pH 1-13 with 50 to 60 mV/pH slope. The electrode maintained the pH response without appreciable slope drift for 170 days if stored in deionized water. The electrode surface can be renewed reproducibly by simple grinding process whenever contaminated or deactivated.

Key Words : Hydrogen ion selective electrode, Composite electrode, Iridium oxide

Introduction

Despite of distinctive performance in wide range of applications of the glass membrane pH electrode the drawbacks are fragility, easy of fouling and lack of surface renewability especially in long-term measurements such as water quality monitoring systems. Polymeric membrane ion-selective electrodes show similar problems except the fragility. They are not fragile but easy to be torn. One of the approaches for the improvement of ruggedness of pH electrode is the utilization of metal oxides such as TiO_2, RuO_2, RhO_2, SnO_2, Ta_2O_5, OsO_2, PtO_2 or IrO_2.[1,2] pH sensing electrodes based on the metal oxides are prepared by thermal or electrochemical deposition of oxide films on the surface of their mother metals or conducting inert metals. They are mostly inert and rugged in harsh applications. Nevertheless surface renewable pH electrode is desired for on-line monitoring systems like telemetric water quality monitoring systems where anti-fouling of the sensing elements is critical.

Among the metal oxide-based pH electrodes iridium oxide-based pH electrode has been extensively studied because of its outstanding behavior among the metal oxides. Thermally prepared iridium oxide-based pH electrodes shows quite close value of 59 mV/pH unit according to the following one electron reaction schemes.[3,4]

$$IrO_2 + H^+ + e^- \rightarrow IrO{\cdot}OH \quad (1)$$

$$2IrO_2 + 2H^+ + 2e^- \rightarrow Ir_2O_3 + H_2O \quad (2)$$

Recently a micro-sized iridium oxide thin film electrode was prepared by sputtering technique for pH sensing in brain tissue or blood.[5] A thick film IrO_2-based pH electrode on the surface of Ir metal lasting 2.5 years with high stability was developed by carbonate melt oxidation technique.[6] Carbon fiber was also used as a substrate instead of metallic Pt or Ir in the preparation of micro pH sensing electrode.[7] Iridium oxide was deposited by electrochemical oxidation of Na_3IrCl_6 in HCl solution. It suggests other inactive conductors such as graphite or carbon black can be utilized as substrates of IrO_2-based pH sensing electrodes. In this work polymeric modified-carbon composite electrode technique was examined for the preparation of surface renewable pH sensing electrode based IrO_2. Polymeric carbon composite electrode can be modified with IrO_2 micro-particles to get pH sensitivity as well as surface renewability. The surface of the composite electrode can be renewed easily by simple polishing or grinding whenever contaminated or deactivated.[8,9] The followings are about their preparations and analytical characteristics.

Experimental Section

Reagents and instruments. All chemicals were reagent grade and used as received unless otherwise mentioned. Ammonium hexachloroiridate(IV) and polyvinyl chloride were from Aldrich. Ketjen black 600JD (semigraphitic carbon from Akzo Chemie) was ground well with a mortar and pestle after drying, and then stored in a sealed bottle. Aqueous solutions were prepared with deionized water (18 MΩ). In most cases commercial pH buffer solutions having pH=4, 7 and 10 were used for the calibration of pH meter. Otherwise home-made standard buffer solutions were prepared according to the recommended procedures.[10] Tris buffer (0.1 M) was prepared for interference experiments. Electrode potentials were measured versus Ag/AgCl reference electrode (3 M KCl) using a pH meter (Accumet 50 from Fisher Scientifics) at 22 °C.

Electrode preparation. Micro-fine particles of IrO_2 (possibly $IrO_2{\cdot}xH_2O$) were prepared by the hydrolysis of hexachloroiridate at elevated temperature.[11] An appropriate portion of $(NH_4)_2IrCl_6$ was dissolved in 150 mL of deionized water. The pH of resulting reddish brown solution was adjusted to about 8.2 with 0.25 M NaOH and followed by

heating to 95 °C with constant stirring for 30 min under reflux setting in an oil bath. The solution turned to deep blue suspension. For the completion of hydrolysis of iridium complex the solution was cooled down to room temperature, and then the pH was adjusted to the initial pH with NaOH. The processes of pH adjustment and heating were repeated until the pH stabilized to initial pH for the completion of the reaction. The solution was purged with oxygen at 95 °C for two hours with a setting of reflux condenser. The suspension of the hydrolytic product was cooled to room temperature. Well ground carbon black was added to the suspension with vigorous stirring. The mixture was sonicated frequently to disperse carbon black completely. Addition of small amount of ethanol was helpful for better dispersion of carbon black. The mixture was stirred overnight. The solid portion of the mixture was separated by filtration and dried under vacuum at 100 °C for 4 hours and followed by calcination at 200 °C for several hours under gentle flow of Ar to get IrO_2/carbon black mixture.

The IrO_2/carbon black mixture were added to PVC solution in 30 mL of DMF then mixed thoroughly by stirring vigorously overnight. Sudden addition of large amount deionized water to the mixture separated the solid components from DMF. The solid mixture was washed thoroughly with deionized water then dried at 70 °C overnight. The mixture was pressure molded into IrO_2-modified polymeric composite electrode material at 100 °C. The electrode material was fabricated into electrodes for pH measurements. The surface of the electrode was ground using 2000 grit SiC emery paper. The electrodes were presoaked in pH 7 buffer solution for 12 hours prior to use.

Results and Discussion

It has been known that the pH response of the iridium oxide-based electrodes depends on the preparation methods. Iridium oxides prepared by thermal oxidation or sputtering techniques are predominantly anhydrous oxides showing 59 mV/pH unit according to the reaction (1) or (2). In contrast it is known that electrochemically prepared oxides are predominantly hydrated iridium oxides such as $IrO_2 \cdot 4H_2O$, $Ir(OH)_4 \cdot 2H_2O$, $\{IrO_2(OH)_2 \cdot 2H_2O\}^{2-} \cdot 2H^+$ and show super-Nerntian response of about 90 mV/pH unit.[12,13] The iridium oxide in this work was prepared by wet chemistry followed by low temperature calcination at 200 °C. So it is not clear whether it corresponds to thermal oxidation product or not. Nevertheless the pH responses of the iridium oxide composite electrodes ranged from 50 to 60 mV/pH unit depending on the batch prepared as shown in Figure 1. They are quite close to the ideal value of 59 mV/pH unit. Initial conditioning of the electrode in pH 7 buffer solution for prolonged period improved the pH response characteristics probably due to the rearrangement of the freshly produced oxide surface by solvation. It has been known that the electrodes prepared by sputtering or thermal oxidation techniques exhibit an aging effect showing negative drift of the electrode potential with time owing to the hydration of the oxide surface in earlier work.[4,14] Accelerated aging of the surface by heating in water at elevated temperature and pressure for prompt stability was demonstrated by Katsube *et al.*[15]

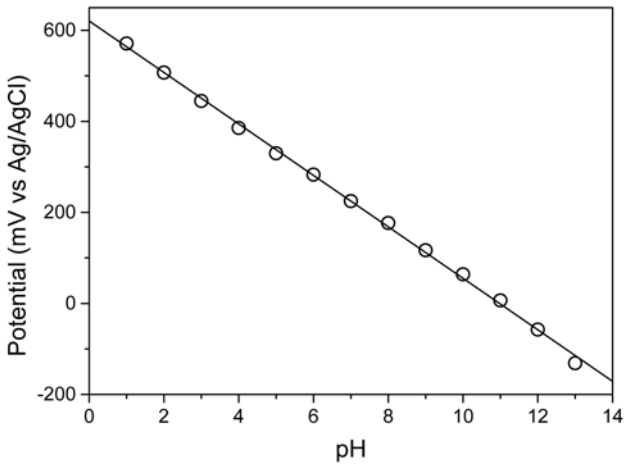

Figure 1. pH dependence of IrO_2-modified composite electrode. The pH was measured against freshly prepared standard buffer solutions.

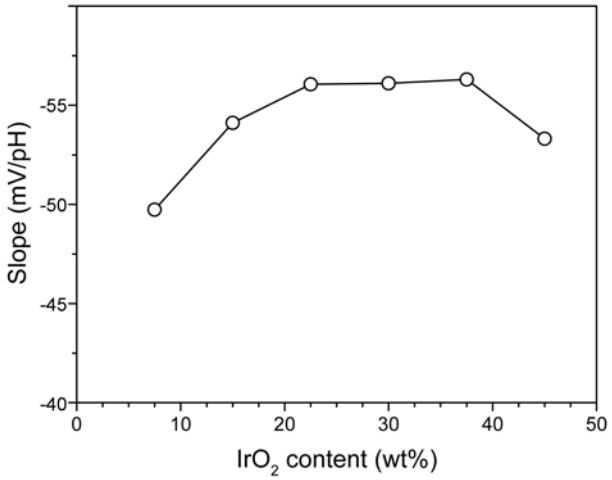

Figure 2. Effect of IrO_2 content in the electrode matrix on the pH response of IrO_2-modified composite electrode.

The content of iridium oxide in the composite electrode matrix affected the pH dependence of the electrode as shown in Figure 2. The pH response of the electrode appeared to be higher than 50 mV/pH in most cases. The pH dependence increased as the iridium oxide content increased, and then leveled off between 20 to 37.5 wt%. The physical strength of the electrodes containing iridium oxide higher than 40% was not good enough to insure the applicability of the electrode. The electrode response also became worse. The electrode containing 22.5 wt% of iridium oxide was selected for further evaluation of the electrochemical characteristics.

The interference characteristics of typical cations and anions were evaluated. The electrode potential in pH 7 Tris buffer solution was measured. Then a specific amount of a salt corresponding to an ion was added and followed by

Table 1. Effect of ions on the pH response of the IrO_2-modified composite electrode

ion	concentration tested (M)	electrode potential (*vs* Ag/AgCl)	
		without ion (mV)	with ion (mV)
Li^+	0.1	192.9	193.8
Na^+	0.1	193.3	195.0
K^+	0.1	193.2	191.3
F^-	0.1	193.4	189.3
Cl^-	0.1	192.8	190.8
Br^-	0.1	192.2	190.6
I^-	0.1	192.2	189.0
NH_4^+	0.01	193.1	194.0
Mg^{2+}	0.1	192.4	189.1
Ca^{2+}	0.1	191.8	195.0
NO_3^-	0.1	191.2	191.5
SO_4^{2-}	0.1	193.4	189.7
MoO_4^{2-}	0.02	191.4	188.5
$Fe(CN)_6^{4-}$	0.01	192.8	132.4
$Fe(CN)_6^{3-}$	0.01	192.9	315.3
H_2O_2	0.05	192.5	255.8

electrode potential measurement. Between the measurements the electrode was washed with deionized water. The test results are shown in Table 1. None of the typical ions showed any remarkable interference. However the electroactive species affected on the electrode potential dramatically as it can be seen in Table 1. The presence of $Fe(CN)_6^{3-}$ and H_2O_2 shifted electrode potential positively because of their oxidizing characteristics meanwhile $Fe(CN)_6^{4-}$ shifted negatively. In addition the electrode was poisoned by $Fe(CN)_6^{3-}$ or $Fe(CN)_6^{4-}$. So the electrode was ground freshly between measurements for those species. It is noticeable that I^- ion affected on the electrode potential remarkably in acidic condition. Similar trends for metal/metal oxide-based pH electrode were reported by others previously.[1,16]

Response time was defined as the time required for 90% of the final potential. In order to evaluate the response time of the IrO_2 electrode, the pH value of test solution was stepped by quick addition of a certain amount of HNO_3 solution into the test solution with a syringe. During the experiment the test solution was stirred vigorously. It took about two to twelve seconds for the pH change from pH 6 to 2 (t_{90} = 2s and t_{100} = 12s). Wipf *et al*. reported 50 ms of response time for their carbon fiber-iridium oxide microelectrodes.[7] Bezbaruah *et al* reported the response time of 1-17s for acidic, neutral, and alkaline pH for an anodically electrodeposited iridium oxide film electrode. They found t_{90} to be pH dependent.[16]

It has been known the hysteresis of iridium oxide-based electrode is somewhat large compard to the glass pH electrode. Marzouk *et al*. reported very small hysteresis of an anodically electrodeposited iridium oxide film electrode, *i.e.*, 2.5 ± 0.6 mV.[17] Less hysteresis was observed for an anodically electrodeposited iridium oxide electrode.[18] However, it often showed disticntive hysteresis in the case of sputtered iridium oxide film electrodes[18] The hysteresis of the iridium oxide composite electrode was tested using buffers of pH 4, 5, 7, 9 and 10. The electrode was calibrated five times against buffers from low pH to high pH repeatedly. A maximum drift of 5 mV was observed which corresponds to an error of 0.1 pH unit.

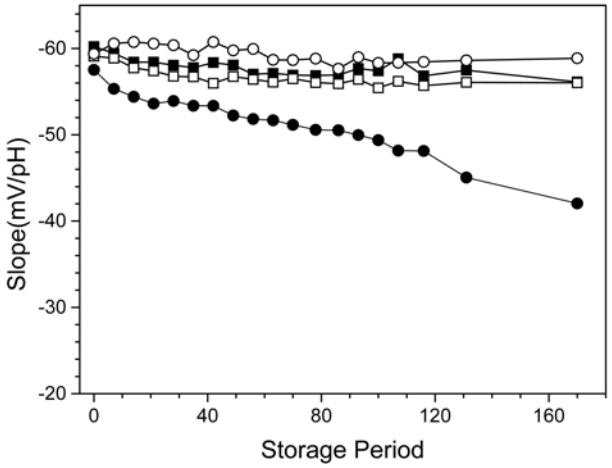

Figure 3. Effect of storage medium on the pH response of IrO_2-modified composite electrode. Open circle: deionized water, solid circle: 4 M KCl, open square: air, solid square: pH 7 buffer.

The storage medium affects on the response of the electrode. Figure 3 shows pH response drift depending on the storage medium. Severe drift in pH response was observed when the electrode was stored in 4 M KCl solution. It is likely due to slow dissolution of iridium oxide from the electrode surface by formation of chloro-iridium complex in the strong chloride solution. So chloride containing medium should be avoided to prevent deactivation of the electrode. Little drift was observed when the electrode stored in air or pH = 7 buffer solution. Long presoak time was required for normal operation when the electrode stored in air. It is not recommended for practical use. The drift of pH response of iridium-based pH electrode has been reported by others.[14,15] However when the electrode was kept in deionized water between measurement the pH response did not drifted noticeably. This behavior is advantageous in practical aspect.

Figure 4 shows the surface renewability of the iridium oxide composite electrode. The electrode surface was ground with 2000 grit SiC paper and then soaked in pH 7 buffer for 12 hours. The potential was measured against pH 4, 7 and 10 buffers. The values of the pH response slope are plotted. The average slope and the relative standard deviation (RSD) appeared to be −55.7 mV/pH and 0.7% respectively for 20 trials. The reproducible surface renewability is one of the biggest advantages because the pH electrode surface can be renewed by simple grinding process whenever it is contaminated or deactivated.

In conclusion a surface renewable iridium oxide-based polymeric composite pH electrode was developed by utilizing composite electrode technique. The electrode showed

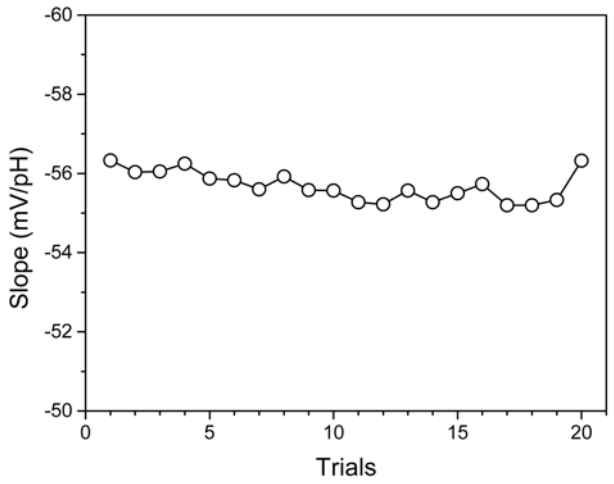

Figure 4. Graph showing the surface renewability of IrO_2-modified composite electrode. The pH response was measured against buffer solutions of pH 4, 7, and 10. The electrode was conditioned in pH buffer solution for 12 hours after each surface renewal.

pH response of 50 to 60 mV/pH and very similar behaviors to the iridium oxide based pH electrode previously reported. The electrode response did not drifted noticeably if stored in deionized water for prolonged period. Furthermore the electrode can be ground simply to get new surface whenever contaminated or deactivated. The utility of this electrode in long-term water quality monitoring system is being examined.

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References

1. Fog, A.; Buck, R. P. *Sens. Actuators* **1984**, *5*, 137.
2. Glab, S.; Hulanicki, A.; Edwall, G.; Ingman, F. *Crit. Rev. Anal. Chem.* **1989**, *21*, 29.
3. VanHoudt, P.; Lewandowski, Z.; Little, B. *Biotech. Bioeng.* **1992**, *40*, 601.
4. Kinoshita, K.; Madou, M. J. *J. Electrochem. Soc.* **1984**, *131*, 1089.
5. Grant, S. A.; Bettencourt, K.; Krulevitch, P.; Hamilton, J.; Glass, R. *Crit. Review Biomed. Eng.* **2000**, *28*, 159.
6. Wang, M.; Yao, S.; Madou, M. *Sens. Actuators B* **2002**, *81*, 313.
7. Wipf, D. O.; Ge, F.; Spaine, T. W.; Baur, J. E. *Anal. Chem.* **2000**, *72*, 4921.
8. Shaw, B. R.; Creasy, K. E. *J. Electroanal. Chem.* **1988**, *243*, 209.
9. Seo, K.; Kim, S.; Park, J. *Anal. Chem.* **1998**, *70*, 2936.
10. *CRC Handbook of Chemistry and Physics*, 83rd ed.; Lide, D. R. Ed.; CRC Press: NY, USA, 2002-2003.
11. Hara, M.; Lean, J. T.; Mallouk, T. E. *Chem. Mater.* **2001**, *13*, 4668.
12. Burke, L. D.; Whelan, D. P. *J. Electroanal. Chem.* **1984**, *162*, 121.
13. Burke, L. D.; Mulcahy, J. K.; Whelan, D. P. *J. Electroanal. Chem.* **1984**, *163*, 117.
14. Kreider, K. G.; Tarlov, M. J.; Cline, J. P. *Sens. Actuators B* **1995**, *28*, 167.
15. Katsube, T.; Lauks, I.; Zemel, J. N. *Sens. Actuators* **1982**, *2*, 399.
16. Bezbaruah, A. N.; Zhang, T. C. *Anal. Chem.* **2002**, *74*, 5726.
17. Marzouk, S. A. M.; Ufer, S.; Buck, R. P.; Johson, T. A.; Dunlap, L. A.; Cascio, W. E. *Anal. Chem.* **1998**, *70*, 5054.
18. Tarlov, M. J.; Semancik, S.; Kreider, K. G. *Sens. Actuators B* **1990**, *1*, 293.