International Journal of Material Science Innovations (IJMSI) 1 (1): 62-72, 2013
ISSN 2289-4063

Review Article

An overview of pH Sensors Based on Iridium Oxide: Fabrication and Application

Saeid Kakooei*, Mokhtar Che Ismail, Bambang Ari-Wahjoedi

Centre for Corrosion Research, Department of Mechanical Engineering, Universiti Teknologi PETRONAS, Tronoh31750, Malaysia
* Corresponding author. Tel.: +60174958196;
E-mail address: skakooei59@hotmail.com

ARTICLE INFO

Article history
Received:01Feb2013
Accepted:10Feb2013

Keywords:
pH Sensor;
Iridium Oxide;
Electrodeposition;
Sputtering;
Sensor Fabrication

A b s t r a c t

In recent years, there has been an increasing interest in the adoption of emerging sensing technologies for instrumentation within a variety of structural systems. Iridium oxide as an stable and interesting material for pH sensor in variuse temperature and pressure was paid attention by a lot of researchers. In this study an overview of different methods for fabrication of IrO_2 pH sensors and their application are presented.

1. Introduction

During the past decades IrO_2 became a superior material for reference electrode[1, 2] and pH measurements in different fields such as biological media [3, 4], food industry [5], nuclear field [6, 7], and oil and gas industry [8-10]. Iridium oxide can provide a rapid and stable response in different media because of its high conductivity and low temperature coefficient. Potentiometric response of the Iridium oxide to pH is a function of transition effect between two oxidation states Ir(III) oxide and Ir(IV) oxide, which can be shown as follow[11]:

$$\text{Ir(IV)oxide} + qH^{+} + ne^{-} \leftrightarrow \text{Ir(III)oxide} + rH_2O$$

In 1996, Roe *et al.*[12] measured dissolved oxygen, pH, and ion currents on mild steel corroded surface using three closely spaced microelectrodes. They proposed a real time mapping of the pH distribution on the mild steel corroded surface.

Two properties of biocompatibility and corrosion resistance of iridium oxide electrodes are noticeable [13]. This fact made iridium oxide electrodes as a potential candidate for Microbial induced corrosion investigation. A crystal structure of stoichiometric iridium oxide is shown in Figure 1.

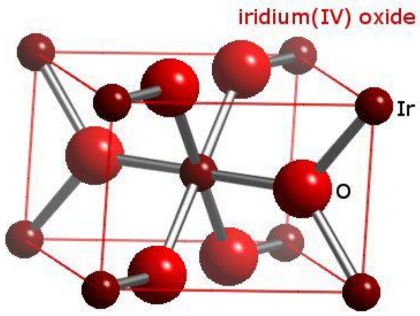

Figure 1: Crystal structure of IrO_2 [14]

The difference between IrO_x pH sensor and traditional glass pH sensor is related to their mechanism for pH measuring. Glass pH electrode depends on solution-phase activities of the relevant electrode whereas IrO_x is dependent on H^+ activity and oxidation state of IrOx. The proposed reaction at the anhydrous Iroquois electrode shown as[15]:

$$2IrO_2 + 2H^+ + 2e^- \leftrightarrow Ir_2O_3 + H_2O \quad (1)$$

And for a hydrous IrO_x electrode as follows reaction:

$$2[IrO_2\,(OH)_2{\cdot}2H_2O]^{2-} + 3H^+ + 2e^- \leftrightarrow [Ir_2O_3(OH)_3{\cdot}3H_2O]^{3-} + 3H_2O \quad (2)$$

Hence the Nernstian response slopes for electrodes prepared by different methods can range between 59 and 88.5 mV/pH. Moreover, proposed Nernst equations are as follows:

$$E=E_0 - 2.3RT/2F \log[Ir_2O_3]/[IrO_2]^2[H^+]^2 \quad (3)$$

and

$$E = E_0 - 2.3RT/2F \log[Ir_2O_3]/[IrO_2]^2[H^+]^3 \quad (4)$$

It be proposed that any variation in the Ir^{3+}/Ir^{4+} ratio, IrO*x* electrode preparation, IrO*x* electrodes age, and deliberate exposure to redox agents such as $Fe(CN)_6^{3-/4-}$ have been shown to affect the pH response [15, 16].

Cathodic storage charge capacities (CSC_C) of the test samples will be calculated by integrating the cathodic area in cyclic voltammograms. The CSC_C data generally be used in the characterization of neural stimulation electrodes [17-19], although in some research work CSC_C calculated like this is approximately equal to the amount of Ir^{4+} on the substrate in thin electrodeposited layers. The calculated area above-mentioned is presented by the CV of an EIROF on Au in Figure 2 [20].

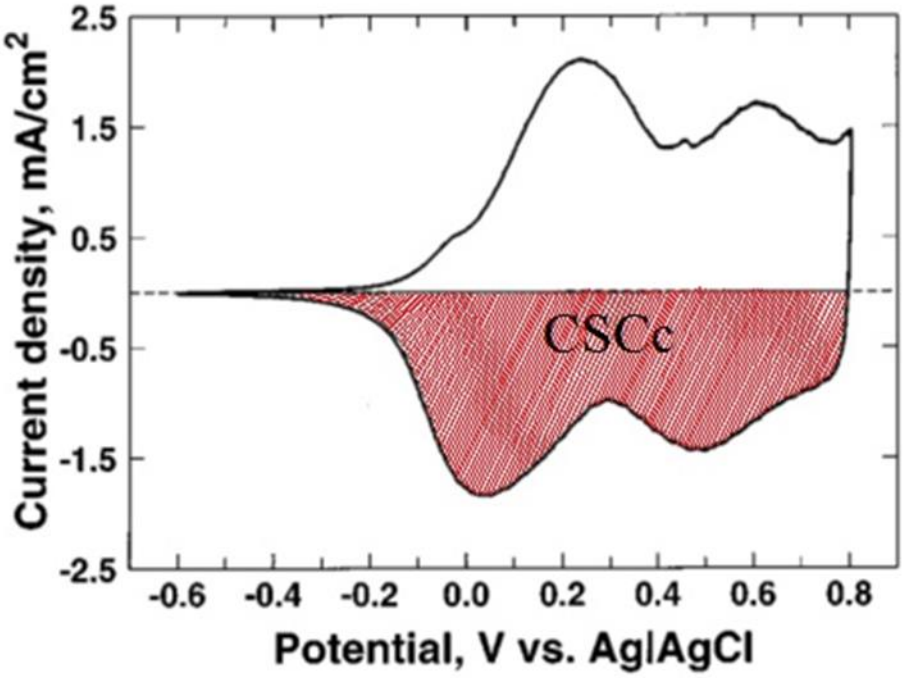

Fig. 2. CV of iridium oxide in PBS at 50 mV/s showing the area used to calculate the CSC of the film [20].

2- Iridium oxide pH sensor fabrication:

It is clear that preparation methods play the main role in the pH response of the iridium oxide-based electrodes. Anhydrous iridium oxides were achieved by thermal oxidation or sputtering Methods which showed pH response of 59 mV/pH, whereas iridium oxides fabricated by electrochemically technique are predominantly hydrated iridium oxides such as $IrO_2{\cdot}4H_2O$, $Ir(OH)_4{\cdot}2H_2O$ which present a super-Nerntian response 90 mV/pH unit [21].

2-1. Sol–gel processes

Sol-gel method was used to fabricated IrO_2 pH sensor on flexible substrate [22, 23]. Three different groups of pH sensors fabricated by the sol-gel process indicated similar near super-Nernstian response, good reversibility, and similar response times, which show better reproducibility and repeatability in this fabrication technique.

The sol-gel technique is well-known as a cheap method for advance material fabrication. Da Silva et al.[24] used a polymeric precursor approach to fabricate a low-cost pH sensor with substitution of IrO_x by TiO_2. The best result was related to 70 % (IrO_x)-30% (TiO_2).

The challenge in sol-gel method is related to the drying process, which led to creating cracks in iridium oxide film due to its dehydration. This phenomenon can be decreased by using proper additives.

2-2. Electrochemical or thermal oxidation of iridium and iridium salts

Song *et al*. [13] fabricated an Ir/IrO_2 pH sensor by using the potentiodynamically cycling method on an Ir electrode in 0.5 M H_2SO_4 aqueous solution at a 50 mV/s scan rate with different exposure time (2, 4, 8, and 24 hr). According to Figure 3, they found that pH sensor fabricated by 2-hr and 4-hr treatment showed more drift than those fabricated by 8-hr and 24-hr treatment.

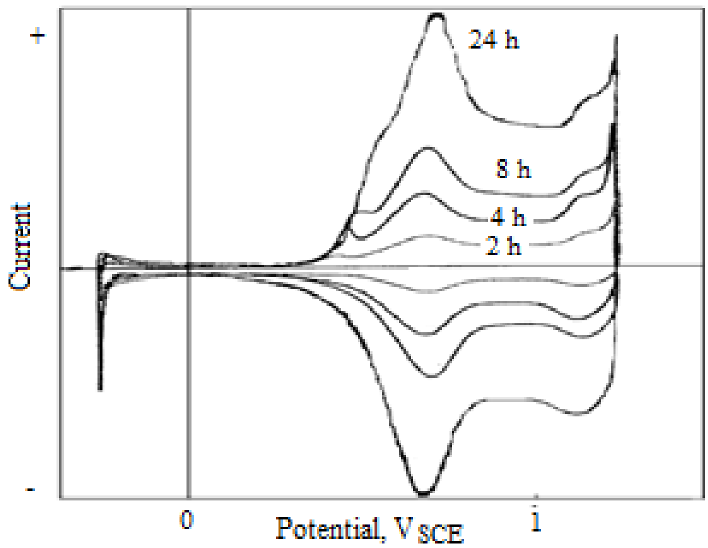

Fig 3. Stacked voltammograms of iridium potentiodynamically cycled between –0.25 V_{SCE} and 1.27 V_{SCE} at 50 mV/s for 2, 4, 8, and 24 hr in deaerated 0.5 M H2SO4 aqueous solution [13].

Song *et al*. investigated the effect of bisulfite and thiosulfate ions on the Ir/IrO_2 pH sensor. The calibration of pH sensor significantly changed when exposed in solution test containing aforementioned ions.

2-3. Sputtering

Sputtering method was used in most IrO2 film fabrication for neural stimulation electrods [17, 25-27]. Kreider [28] in 1991 used sputtered iridium oxide as pH-sensing electrodes in high-temperature high-pressure saline solutions. Sputtered iridium oxide films was fabricated in mixed Argon and oxygen environment in a 1:l ratio at a total pressure of ~0.40 Pa. The thickness of 0.5-0.7 µm thick depositions were made primarily on alumina circuit board at

30-40 °C and at 240 °C. He found that with increasing exposure time in saline solutions, pH sensitivity decreased at high temperature. The main disadvantage of sputtering method is expensive price of its target price which is not also available for some rare material.

2-4. Anodic or cathodic electrodeposition

Yamanaka [29] proposed electrodeposition of iridium oxide for the first time for fabrication of display device. His suggested solution was based on a complex of $IrCl_4$ and oxalate component. After that a lot of researcher improved this solution or used it as described by Yamanaka [18, 30-32].

Ryynänen *et al.* for first time used atomic layer deposition (ALD) for iridium oxide (IrO_x) fabrication as the pH sensitive layer with an average sensitivity of -67 mV/pH at 22 °C. They could coat 110 nm IrO_x layer on a glass substrate consists of 300 nm thick titanium electrodes. Their pH sensor was able to detect pH in a range from pH 4 to pH 10 [33].

Various metals have been used as substrate for IrO_2 coating such as Au, Pt, Ir, PtIr, stainless steel, tin-doped indium oxide (ITO) [29, 34, 35]. Marzouk [36] in a valuable work investigated various substrate pure metals such as Au, Ag, Ti, Cu, Ni, W, Zr, and Co and some alloys such as nickel-chrome, Hastelloy and stainless steel. The blue layer of deposit, proper adhesion of deposit to surface, and stability of the cyclic voltammogram were the most important factor for substrates comparing. Mayorga *et al.* [35, 37] described a simple pH sensor fabrication through IrO_2 electrodeposition on stainless steel substrate. The fabricated sensor had fast response time and good repeatability.

Most of researchers followed original Yamanaka solution[29], although some others attempted the modification of his solution[38, 39].

Marzouk approved that using $(NH_4)_2[IrCl_6]$ instead of $IrCl_4$ was wrong since the solution did not develop to dark greenish-blue color for up to 7 days at room temperature [36]. Marzouk was successful to reduce the development time of solution from 3 days to 10 minutes by heating the solution to 90 °C. Petit et al. [38] replaced $IrCl_4$ with K_3IrCl_6. The required time for solution development was 4 days at 35 °C. This solution did not offer any highlighted merit. Lu *et al.* [18] attempted to use $H_2IrCl_6.6H_2O$ for electrodeposition solution. Their solution was developed from light yellow to dark blue after 5 days.

Table 1. Application and characterization of IrO_2 electrodes fabricated by electrodeposition technique.

Substrate	Precursor materials	Oxide thickness	Sensitivity (Nernstian behavior mV/pH)	Application	References
Platinum wire	---------	---------	70.2	Interfacial pH measurement	[39]
Au, Pt, Ir, PtIr, and 316LVM stainless steel wires	$IrCl_4$, oxalic acid, and K_2CO_3	100 nm	---------	Neural stimulation and recording	[34]
Tin-doped indium oxide (ITO)	$IrCl_4$, oxalic acid, and K_2CO_3	---------	---------	Electrochromic display devices	[29]
Platinum	$IrCl_4$, oxalic acid, and K_2CO_3	---------	-68 to -77	Glucose sensor	[1]
Au, Ag, Ti, Cu, Ni, W, Zr, Co, nickel-chrome, Hastelloy and stainless steel	$IrCl_4$, oxalic acid, and K_2CO_3	---------	-73	pH measurement as a detector in a flow injection analysis (FIA) system	[36]
Platinum	$H_2IrCl_6 \cdot 6H_2O$, oxalic acid, and K_2CO_3	---------	−75.51	pH measurement as a Neural sensor	[18]
Stainless steel	$IrCl_4$, oxalic acid, and K_2CO_3	20-30 nm	---------	pH measurement as a biosensor	[35, 37]
SnO2-coated glass	K_3IrC1_6, oxalic acid, and K_2CO_3	--------	---------	---------	[38]
Polyimide-Cr-Au	$IrCl_4$, oxalic acid, and K_2CO_3	--------	77	pH measurement in brain tissues	[40]
ITO-coated glass	$IrCl_4$, oxalic acid, and K_2CO_3	--------	64.5	----------	[11]
Carbon fiber	Na_3IrCl_6, HCl, NaOH	--------	---------	Scanning electrochemical microscope (SECM)	[41]
Sputtered Platinum on flexible Kapton films	$IrCl_4$, oxalic acid, and K_2CO_3	--------	-63.5	pH measurement of extracellular Myocardial Acidosis during Acute Ischemia	[42]
Platinum	$IrCl_4$, oxalic acid, and K_2CO_3	--------	−77.6	pH measurement of microfluidic-based microsystems	[32, 43]
Sputtered Gold on Si wafer	$IrCl_4$, oxalic acid, and K_2CO_3	--------	-68	Monitoring of water quality	[15]
Stainless steel	$IrCl_4$, oxalic acid, and K_2CO_3	--------	-73	Corrosion monitoring	[44]

Nguyen *et al.* [40] observed a 12 mV/pH as drift of sensitivity after 8 days sensitivity test repeating. They explained that this change in sensitivity is due to dehydration phenomenon of hydrated iridium oxide, which can be minimized by keeping IrO_2 pH sensor in phosphate buffered saline (PBS) solution.

Wipf et al.[41] produced a pH microelectrode via electrodeposition of IrO_2 on carbon fiber. They used this pH sensor in development of the scanning electrochemical microscope (SECM). The fabricated pH sensor was able to measure pH near a surface. The result was shown as a vertical pH map or image.

As Lu et al.[18] reported there is an optimum thickness for IrO_2 electrodeposited coating. Coating electrochemical performance increase when its CSC_c and thickness increase, but when CSC_c approach to ~45mC/cm^2 delamination of IrO_2 coating was detected. Their demonstarated iridium oxide electrode showed a pH sensitivity -75.51 mV/pH in broad pH range of 1-13. More research works are presented in Table 1 with electrode application and other characterization.

2-5. Other methods

A surface renewable IrO_2 pH sensor or hydrogen ion-selective electrode can be made by using composite electrode technique. Quan et al.[21] used carbon black, polyvinyl chloride and ammonium hexachloroiridate to fabricate an IrO_2 based composite electrode. Increasing IrO_2 content up to 40 wt% showed an increasing on the pH response. They also investigated the effect of different ions on pH electrode efficiency that resulted that $Fe(CN)_6^{3-}$, $Fe(CN)_6^{4-}$, I^-, and H_2O_2 affected by electrode result. Similar results for IrO_2 pH sensor were also reported in other research [45].

Park et al.[46, 47] fabricated an iridium oxide-glass composite electrode by mixing ammonium hexachloroiridate and glass powder, pressing, and sintering under oxygen atmosphere. The mention electrode was renewable by using 2000 grit SiC emery paper whenever it becomes fouled or deactivated. They observed many microscopic voids in the electrode surface after sintering at high temperature. pH response in these electrodes was dependent on the size and population of voids. Surface voids can be reduced by hot press sintering technique.

3. Applications

3.1. Biomedical and Biological applications

Marzouk et al.[48] in 2002 measured extracellular pH in ischemic rabbit papillary muscle for the first time. They used a pH sensor based on an IrO_2 film electrodeposited on a planar sputtered platinum electrode fabricated on a flexible Kapton substrate.

Fast response time of pH sensor is very important for biological application. Iridium oxide pH microsensors were used to measure the acidification rate of CHO and fibroblast cells in a cell culture with microfluidic control [32]. This approach can also be used in bioanalytical filed or biosensor [32, 43].

Iridium oxide sensors are widely used in neural stimulation and recording electrodes regarding to their low impedance, high charge storage capacity [34].

Iridium oxide based pH sensor is a reliable and robust approach for biological application. O'Hare et al. [4] investigated application of IrO_2 electrode fabricated by thermal oxidation and anodization as a pH sensor in the cultured intervertebral disc. Their electrodes were tending to be unstable in physiological media. Also dissolution of the hydrated oxide film happened in higher concentrations of chloride. They reduced the effect of chloride by using thermally annealed Nafion films. Although Nafion film caused an increase in response time, it could protect iridium oxide film against the aggressive nature of biological media [32, 42].

3.2. Industrial applications

Zhang et al.[39, 49] used IrO_2 pH sensor for measuring pH in electrode/solution interface in electrodeposition process. They found that by increasing the applied potential, interfacial pH increased. Marzouk [36] fabricated a tubular IrO_2 pH sensor for using in a flow injection analysis (FIA) system as a detector.

The pH of a solution is one of the most important parameters used for characterizing an electrolyte during corrosion processes [5, 8, 10]. For this purpose, some researcher used iridium oxide microelectrode to study the effect of local pH near the surface on corrosion on steel surfaces [9, 50].

4. Conclusion

In this study various techniques for fabrication of IrO_2 electrode was presented. Iridium oxide pH sensor are able to measure pH changes in real-time which enablae researchers to use it in variouse industrial field. More attention was paid to electrodeposition method due to cheaper fabrication process, low-temperature process, potential for using cheaper substrates, and versatility of sensor shapes and designs.

Acknowledgements

We are gratefully acknowledge the financial support from Ministry of Higher Education (ERGS Grant No: 158200327) and Universiti Teknologi PETRONAS that has made this work possible.

References

1. Yang, H., S.K. Kang, D.H. Shin, H. Kim, and Y.T. Kim. 2003. IEEE.
2. Franklin, R.K., S. Joo, S. Negi, F. Solzbacher, and R.B. Brown. 2009. IEEE.
3. Macur, R.A., Iridium-Iridium oxide electrode for measuring pH of blood and other fluids, 1973, US Patent 3,726,777.
4. O'Hare, D., K.H. Parker, and C.P. Winlove, Metal–metal oxide pH sensors for physiological application, Medical engineering & physics. 2006, 28(10): 982-988.
5. Chiao, J.C. and W.D. Huang, Amorphous IrOx film pH sensor, US Patent App. 12/911,329, 2010.
6. Huang, P. and K.G. Kreider, Electrochemical evaluation of solid state pH sensors for nuclear waste containment, 1988, Nuclear Regulatory Commission, Washington, DC (USA). Div. of Engineering; National Bureau of Standards, Washington, DC (USA). Center for Chemical Engineering.
7. Kreider, K., Iridium oxide thin-film stability in high-temperature corrosive solutions, Sensors and Actuators B: Chemical. 1991, 5(1–4): 165-169.
8. Prasad, R., Assessment and Control of MIC in the Oil Industry in the 20th Century, CORROSION 2000. 2000.
9. Lewandowski, Z., T. Funk, F. Roe, B.J. Little, J. Kearns, and B. Little, Spatial distribution of pH at mild steel surfaces using an iridium oxide microelectrode, ASTM SPECIAL TECHNICAL PUBLICATION. 1994, 1232: 61-61.
10. Little, B.J., Z. Lewandowski, T. Funk, and F. Roe, Spatial Distribution of pH at Mild Steel Surfaces Using an Iridium Oxide Microelectrode, 1994, DTIC Document.
11. Kim, Y.J., Y.C. Lee, B.K. Sohn, J.H. Lee, and C.S. Kim, A novel pH microsensor with a built-in reference electrode, Journal Korean Physical Society. 2003, 43(1): 769-772.
12. Roe, F., Z. Lewandowski, and T. Funk, Simulating microbiologically influenced corrosion by depositing extracellular biopolymers on mild steel surfaces, Corrosion. 1996, 52(10).
13. Song, I., K. Fink, and J. Payer, Metal oxide/metal pH sensor: Effect of anions on pH measurements, Corrosion. 1998, 54(01).
14. Arikawa, T., Y. Takasu, Y. Murakami, K. Asakura, and Y. Iwasawa, Characterization of the structure of RuO_2-IrO_2/Ti electrodes by exafs, The Journal of Physical Chemistry B. 1998, 102(19): 3736-3741.
15. Carroll, S. and R.P. Baldwin, Self-Calibrating Microfabricated Iridium Oxide pH Electrode Array for Remote Monitoring, Analytical chemistry. 2010, 82(3): 878-885.
16. Kurzweil, P., Metal oxides and ion-exchanging surfaces as pH sensors in liquids: State-of-the-art and outlook, Sensors. 2009, 9(6): 4955-4985.

17. Thanawala, S.S., R.J. Baird, D.G. Georgiev, and G.W. Auner, Amorphous and crystalline IrO_2 thin films as potential stimulation electrode coatings, Applied Surface Science. 2008, 254(16): 5164-5169.
18. Lu, Y., T. Wang, Z. Cai, Y. Cao, H. Yang, and Y.Y. Duan, Anodically electrodeposited iridium oxide films microelectrodes for neural microstimulation and recording, Sensors and Actuators B: Chemical. 2009, 137(1): 334-339.
19. Cogan, S., P. Troyk, J. Ehrlich, T. Plante, D. McCreery, and L. Bullara. 2003. IEEE.
20. Ross D. Meyer, S.F.C., Member, Trung H. Nguyen, R. David Rauh, Electrodeposited Iridium Oxide for Neural Stimulation and Recording Electrodes, IEEE TRANSACTIONS ON NEURAL SYSTEMS AND REHABILITATION ENGINEERING. 2001, 9(1): 2-11.
21. Quan, H., W. Kim, K. Chung, and J. Park, Surface renewable hydrogen ion-selective polymeric composite electrode containing iridium oxide, Bulletin Korean Chemical Society. 2005, 26(10): 1565.
22. Huang, W.D., J. Wang, T. Ativanichayaphong, M. Chiao, and J. Chiao. 2008. Society of Photo-Optical Instrumentation Engineers.
23. Huang, W.D., L.C. Hsu, J. Wang, T. Ativanichayaphong, S. Deb, M. Chiao, and J. Chiao. 2008. Society of Photo-Optical Instrumentation Engineers.
24. Da Silva, G., S. Lemos, L. Pocrifka, P. Marreto, A. Rosario, and E. Pereira, Development of low-cost metal oxide pH electrodes based on the polymeric precursor method, analytica chimica acta. 2008, 616(1): 36-41.
25. Van Ooyen, A., G. Topalov, G. Ganske, W. Mokwa, and U. Schnakenberg, Iridium oxide deposited by pulsed dc-sputtering for stimulation electrodes, Journal of Micromechanics and Microengineering. 2009, 19(7): 074009.
26. Lee, I.-S., C.-N. Whang, J.-C. Park, D.-H. Lee, and W.-S. Seo, Biocompatibility and charge injection property of iridium film formed by ion beam assisted deposition, Biomaterials. 2003, 24(13): 2225-2231.
27. Wessling, B., A. van Ooyen, W. Mokwa, and U. Schnakenberg. Engineering in Medicine and Biology Society, 2006. EMBS'06. 28th Annual International Conference of the IEEE. 2006. IEEE.
28. Kreider, K., Iridium oxide thin-film stability in high-temperature corrosive solutions, Sensors and Actuators B: Chemical. 1991, 5(1): 165-169.
29. Yamanaka, K., Anodically Electrodeposited Iridium Oxide Films(AEIROF) from Alkaline Solutions for Electrochromic Display Devices, Japanese journal of applied physics. 1989, 28(part 1): 632-637.
30. Pikulski, M. and W. Gorski, Iridium-based electrocatalytic systems for the determination of insulin, Analytical chemistry. 2000, 72(13): 2696-2702.
31. Terashima, C., T.N. Rao, B.V. Sarada, N. Spataru, and A. Fujishima, Electrodeposition of hydrous iridium oxide on conductive diamond electrodes for catalytic sensor applications, Journal of Electroanalytical Chemistry. 2003, 544: 65-74.
32. Ges, I.A., B.L. Ivanov, D.K. Schaffer, E.A. Lima, A.A. Werdich, and F.J. Baudenbacher, Thin-film IrOx pH microelectrode for microfluidic-based microsystems, Biosensors and Bioelectronics. 2005, 21(2): 248-256.
33. Ryynänen, T., K. Nurminen, J. Hämäläinen, M. Leskelä, and J. Lekkala, pH electrode based on ALD deposited iridium oxide, Procedia Engineering. 2010, 5: 548-551.

34. Meyer, R.D., S.F. Cogan, T.H. Nguyen, and R.D. Rauh, Electrodeposited iridium oxide for neural stimulation and recording electrodes, Neural Systems and Rehabilitation Engineering, IEEE Transactions on. 2001, 9(1): 2-11.

35. Mayorga Martinez, C.C., R.E. Madrid, and C.J. Felice, Electrochemical and geometrical characterization of iridium oxide electrodes in stainless steel substrate, Sensors and Actuators B: Chemical. 2008, 133(2): 682-686.

36. Marzouk, S.A.M., Improved electrodeposited iridium oxide pH sensor fabricated on etched titanium substrates, Analytical chemistry. 2003, 75(6): 1258-1266.

37. Martinez, C.C.M., R.E. Madrid, and C.J. Felice, A pH Sensor Based on a Stainless Steel Electrode Electrodeposited With Iridium Oxide, Education, IEEE Transactions on. 2009, 52(1): 133-136.

38. Petit, M.A. and V. Plichon, Anodic electrodeposition of iridium oxide films, Journal of Electroanalytical Chemistry. 1998, 444(2): 247-252.

39. Zhang, J.M., Q. Shi, C. Yang, and Q.F. Dong, In-situ pH measurement at the electrode/solution interface, Chinese Chemical Letters. 2000, 11(7): 617-620.

40. C. M. Nguyen, H.C., W. D. Huang, and J.-C. Chiao, An Electro-Deposited IrOx Thin Film pH Sensor, in BMES Biomedical Engineering Society Annual Meeting2011: Hartford.

41. Wipf, D.O., F. Ge, T.W. Spaine, and J.E. Baur, Microscopic measurement of pH with iridium oxide microelectrodes, Analytical chemistry. 2000, 72(20): 4921-4927.

42. Marzouk, S.A.M., S. Ufer, R.P. Buck, T.A. Johnson, L.A. Dunlap, and W.E. Cascio, Electrodeposited iridium oxide pH electrode for measurement of extracellular myocardial acidosis during acute ischemia, Analytical chemistry. 1998, 70(23): 5054-5061.

43. Ges, I.A., B.L. Ivanov, A.A. Werdich, and F.J. Baudenbacher, Differential pH measurements of metabolic cellular activity in nl culture volumes using microfabricated iridium oxide electrodes, Biosensors and Bioelectronics. 2007, 22(7): 1303-1310.

44. Kakooei, S., M.C. Ismail, and B.A. Wahjoedi, Electrochemical Study of Iridium Oxide Coating on Stainless Steel Substrate, Int. J. Electrochem. Sci. 2013, 8: 3290-3301.

45. Bezbaruah, A.N. and T.C. Zhang, Fabrication of anodically electrodeposited iridium oxide film pH microelectrodes for microenvironmental studies, Analytical chemistry. 2002, 74(22): 5726-5733.

46. Park, J., J. Kim, and H. Quan, A surface renewable iridium oxide-glass composite hydrogen ion electrode, Microchemical Journal. 2010, 95(1): 102-106.

47. Park, J.M. and J.Y. Kim, Surface Renewable Iridium Oxide-Glass or Ceramic Composite Hydrogen Ion Electrode, US Patent App. 12/846,791, 2010.

48. Marzouk, S.A.M., R.P. Buck, L.A. Dunlap, T.A. Johnson, and W.E. Cascio, Measurement of extracellular pH, K+, and lactate in ischemic heart, Analytical biochemistry. 2002, 308(1): 52-60.

49. Zhang, J., C. Lin, Z. Feng, and Z. Tian, Mechanistic studies of electrodeposition for bioceramic coatings of calcium phosphates by an in situ pH-microsensor technique, Journal of Electroanalytical Chemistry. 1998, 452(2): 235-240.

50. Tanabe, H., K. Togashi, T. Misawa, and U. Kamachi Mudali, In situ pH measurements during localised corrosion of type 316LN stainless steel using scanning electrochemical microscopy, Journal of materials science letters. 1998, 17(7): 551-553.