

SUPER-NERNSTIAN POTENTIOMETRIC pH SENSOR BASED ON THE ELECTRODEPOSITION OF IRIIDIUM OXIDE NANOPARTICLES

Munawar Khalil^{1*}, Ning Liu², Robert L. Lee³

¹*Department of Chemistry, Faculty of Mathematics and Natural Sciences, Universitas Indonesia, Kampus UI Depok, Depok 16424, Indonesia*

²*Department of Petroleum Engineering, University of Louisiana at Lafayette, 70504 Louisiana, USA*

³*Petroleum Recovery Research Center, New Mexico Institute of Mining and Technology, Socorro, New Mexico 87801, USA*

(Received: January 2018 / Revised: February 2018 / Accepted: March 2018)

ABSTRACT

This work reports an investigation into the synthesis and electrodeposition of iridium oxide nanoparticles to fabricate an Au-based super-Nernstian potentiometric pH sensor. Monodisperse ultrafine iridium oxide nanoparticles with a mean particle diameter of 1–2 nm were successfully synthesized by the facile alkaline hydrolysis method and electrodeposited on the surface of Au substrate using Cyclic Voltammetry (CV). Based on the result, it was observed that the iridium oxide deposited Au substrate had a rough surface morphology. It was also found that the as-prepared sensor exhibited an excellent pH sensitivity and good stability over a long period, with a super-Nernstian response value of -73.7 mV/pH.

Keywords: Cyclic voltammetry; Electrodeposition; Iridium oxide; pH sensor; Super-Nernstian

1. INTRODUCTION

Accurate measurement of pH has been widely considered to be one of the pivotal parameters in many industrial processes. This is mainly due to the numerous biological and chemical reactions that are important in different fields; biomedical and tissue engineering, food and pharmaceutical industries, and oil and gas applications are all pH dependent. Currently, accurate determination of pH can be conveniently carried out using a pH meter, which is generally equipped with a conventional glass-type electrode. However, utilization of such devices has been widely reported to be inefficient in several applications, such as in *in vivo* biomedical applications, extreme conditions at oil and gas wells, or in clinical or food monitoring systems, due to its lack of deformability, electrode brittleness and the limitation of electrode size (Glab et al., 1989; Wang et al., 2002; Elsen et al., 2009; Huang et al., 2011). Furthermore, it is also reported that glass type electrodes present several disadvantages, such as instability in the measurement of alkaline and flouridic acid solutions; difficulties in their construction; high output impedance; low response time; and being easy to break (Yao et al., 2001; Martinez et al., 2009; Khalil et al., 2016). Alternatively, metal-based pH electrodes are considered to be one of the most potential candidates for accurate and reliable pH measurement in such applications.

Several types of metal substrates have been widely studied for application in the fabrication of potentiometric pH sensing electrodes. Among these, stainless steel and Au are the most

*Corresponding author's email: mkhalil@sci.ui.ac.id, Tel: +62-21-7270027, Fax: +62-21-7863432
Permalink/DOI: <https://doi.org/10.14716/ijtech.v9i3.1263>

common types of metal substrate to be used, owing to their chemical durability and high responses (Huang et al., 2014; Kim & Yang, 2014; Nguyen et al., 2015). Recent studies have also reported that coating of metal substrates with a thin film of metal and transition metal oxides could be made to increase pH-responsive sites with high H⁺ selectivity and to improve the metal substrate durability (Subasri et al., 2012; Xu et al., 2014). For instance, Hashimoto et al. have investigated the utilization of 3d-block metal oxides (MO_x, where M = Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu and Zn) as a thin film coating material for stainless steel for pH sensing electrodes, via the sol-gel dip-coating method (Hashimoto et al., 2016). Based on their results, it is reported that the metal oxide based electrode exhibited a much shorter response time than commercial glass electrodes, and showed excellent pH sensitivity and repeatability. Other studies have shown that several types of transition metal oxides, such as PtO₂, IrO₂, RuO₂, OsO₂, Ta₂O₅, TiO₂, MnO₂, Co₃O₄, NiO, CuO, ZnO, WO₃ and CeO₂, have been shown to be good candidates for thin film coating in the fabrication of metal based pH sensing electrodes (Hashimoto & Yoko 1995; Qingwen et al., 2000; Charchour et al., 2011; Manjakkal et al., 2015).

In general, iridium oxide has been widely preferred as a coating material for pH sensors due to its stability against dissolution, potential, chemical stability over a wide range of temperatures (up to 250°C), fast response, low sensitivity towards ions or redox interferences, and wide pH response range (Marzouk et al., 1998; Xu et al., 2010). Because of these benefits, iridium oxide coated metal-based pH electrodes have been investigated for various applications, such as Severinghaus-type CO₂ sensors for oil and gas applications; micro-environmental studies; microsystems for cell culture; and biomedical applications (Yao & Wang, 2002; Ges et al., 2007; Johnson et al., 2007). Recent work has also reported the electrodeposition of iridium oxide nanoparticles on stainless steel substrate for pH sensing electrodes (Khalil et al., 2016). It was observed that the as-prepared pH sensing electrodes displayed an excellent pH sensitivity and reliability with super-Nernstian behavior, with a pH sensitivity value of -72.6 mV/pH.

Nevertheless, other studies have shown that the utilization of stainless steel as metal substrate for the fabrication of pH sensing electrodes poses several challenges, such as the response being easily affected by Cl⁻ ions, and its lack of stability in extreme conditions; for instance, in the extreme temperatures, pressure, contamination and salinity of oil and gas wells (Subasri et al., 2015; Xu et al., 2014). Therefore, the application of Au as metal substrate in the fabrication of a super-Nernstian pH sensing electrode is studied in this work. Iridium oxide nanoparticles were synthesized by the facile alkaline hydrolysis method and employed as the deposition solutions using cyclic voltammetry. The as-synthesized nanoparticles were characterized by various characterization methods, such as UV/Vis spectroscopy and Transmission Electron Microscope (TEM), while the deposited Au-based electrodes were characterized using Scanning Electron Microscope-Energy Dispersive Spectroscopy (SEM-EDS). Finally, the sensing abilities of the electrodes were studied by investigating their static and dynamic properties, such as sensitivity, calibration, time response and stability.

2. EXPERIMENTAL METHODS

2.1. Materials

Gold (Au) wire (diameter: 0.25 mm) was purchased from Alfa-Aesar and used as the metal substrate. Potassium hexachloroiridate(III) (K₂IrCl₆) and HNO₃ (70%) were purchased from Sigma-Aldrich and used as the precursors for the synthesis of iridium oxide nanoparticles. NaOH, HCl and pH buffer solution series were purchased from Fischer Scientific and used in the sensing abilities measurements. For the preparation of the Phosphate Buffer Saline (PBS) solution, KH₂PO₄ (purchased from Alfa Aesar), and K₂HPO₄ and NaCl (purchased from Sigma-Aldrich) were used.

2.2. Synthesis of Iridium Oxide Nanoparticles

Iridium oxide nanoparticles were synthesized via the alkaline hydrolysis method and used as the deposition solution in the electrodeposition of the Au metal substrate using Cyclic Voltammetry (CV) (Zhao et al., 2011a; Khalil et al., 2016). In this method, 10 wt% of NaOH was slowly added to 2.0 mM aqueous K_2IrCl_6 solution until the final mixture became yellow and had a pH of 13. The resulting solution was then heated at 90°C for 20 minutes and allowed to cool to room temperature. The solution was then kept in an ice bath to obtain a blue solution. With vigorous stirring, the pH of the solution was adjusted to pH 1 by the rapid addition of 3 M HNO_3 . The mixture was then further stirred for 80 minutes until the solution became deep blue and it was finally stored in a refrigerator at 2°C.

2.3. Electrode Preparation

The electrodes were prepared by cutting the metal substrate (Au) wire to about 5 cm in length and polishing its surface using sandpaper to roughen it. The metal substrate was then ultrasonically rinsed using acetone and deionized water to remove any possible contaminants. To fabricate the pH sensing electrode, iridium oxide nanoparticles were electrodeposited onto the Au surface using Cyclic Voltammetry (CV). The experiments were carried out with a Solartron Analytical 1470E CellTest System with Solartron Analytical 1242A frequency response analyzer. The data visualization and processing were carried out with CellTest v5.2.0. In this case, a three electrode cell system was used, in which Au was the working electrode, and Ag|AgCl and Pt were the reference and counter electrodes, respectively. A triangular wave CV method between -0.5 to 0.65 V (vs. Ag|AgCl) was applied at a 200 mV/s scan rate for 500 cycles in colloidal iridium oxide nanoparticles as the electrodeposition solution at pH 13. Following the procedure, the electrodes were rinsed with deionized water and stored in a pH 7 buffer solution. For the Cathodic Charge Storage capacity (CSCc) measurement, CV was carried out between -0.6 to 0.8 V (vs. Ag|AgCl) at a 50 mV/s scan rate in a pH 7.2 PBS solution. This solution was prepared by mixing 11.1 ml of 1M KH_2PO_4 , 38.9 ml of 1M K_2HPO_4 and 30 ml of 5M of NaCl, and diluting it with one liter of deionized water. The pH was adjusted to 7.2 using 10 wt% of aqueous NaOH solution.

2.4. Measurements

The as-prepared iridium oxide nanoparticles were analyzed using UV/Vis spectroscopy (Cary® 50 UV-Vis Spectrophotometers from Varian, Inc) and TEM (JEOL 2010 EX Hi-Resolution Transmission Electron Microscope (HRTEM) with Oxford-Link EDS and a Gatan Digital Micrograph equipped with slow scan CCD camera, operated at 200 kV. The surface morphology of the sensing electrode was studied using SEM-EDS (Hitachi S-3200N equipped with PGT Energy Dispersive X-Ray Analyzer). To evaluate the pH sensors, calibration of the sensor with respect to the pH standard was carried out. This was done by Open Circuit Potential (OCP) measurement of each electrode against the Ag|AgCl electrode, as a function of the pH of the buffer solutions. The measurement was made by using an Agilent 34401A Digital Multimeter connected to a PC with Agilent Intuilink Data Capture software, and the OCP was registered once the variations were stable and below 0.05 V for 30 seconds. All measurements were carried out at ambient temperatures.

3. RESULTS AND DISCUSSION

3.1. Synthesis of Iridium Oxide Nanoparticles

In the alkaline hydrolysis method, the formation of ligand free iridium oxide nanoparticles can be easily monitored using UV-Vis spectrometry at 580 nm during the course of the reaction. Earlier studies have reported that both bulk and colloidal iridium oxide absorb strongly at about 580 nm, while the monomeric iridium complex of $[Ir(OH)_6]^{2-}$ has no visible absorbance (Loon & Page, 1966; Zhao et al., 2011a). Figure 1a shows the UV/Vis spectra of the reaction mixture

during the reaction in the synthesis of iridium oxide nanoparticles. In the early course of the reaction, the iridium salt precursors were hydrolyzed to form a yellow $[\text{Ir}(\text{OH})_6]^{2-}$ complex, which could be attributed to a strong absorption at 330 nm. When the pH of the solution was adjusted to pH 1, these complexes underwent a rapid condensation reaction to form colloidal iridium oxide nanoparticles, which strongly absorbed visible radiation at 580 nm. Nevertheless, a previous study has reported that the formation of these colloidal iridium oxide nanoparticles via a rapid condensation reaction at low pH could be partially reversed, to form the corresponding iridium complex in alkaline conditions (Khalil et al., 2016). Figure 1b presents the TEM image for the as-synthesized colloidal iridium oxide nanoparticles. Based on the result, it is clear that the nanoparticles had a uniform dispersity, with a sphere-like shape, and mean particle size of around 1–2 nm. It is also clear that the as-synthesized nanoparticles were severely aggregated with each other since no capping agent was used during the synthesis.

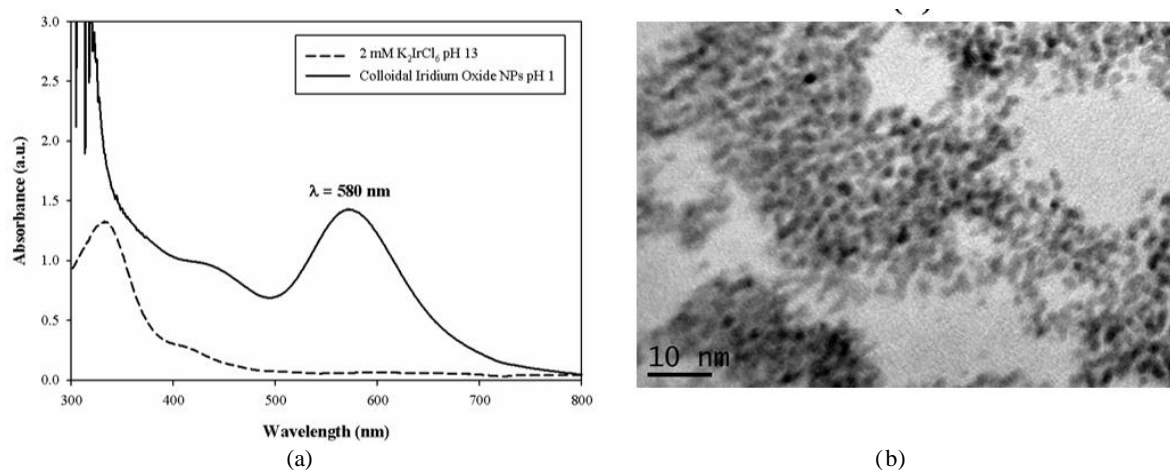


Figure 1 (a) UV-Vis spectra of reaction solutions during the course of the reaction; (b) TEM image of colloidal iridium nanoparticles (scale bar: 10 nm)

3.2. Electrodeposition

Figure 2a shows the typical cyclic voltammogram recorded during the electrodeposition of the ligand free colloidal iridium oxide nanoparticles on the Au metal substrate at pH 13. Based on this result, the voltammogram matches well what has been reported elsewhere (Petit & Plichon, 1989; Chen et al., 2009; Hu et al., 2009). It shows two characteristics redox couples of Ir(III)/Ir(IV) and Ir(IV)/Ir(V) transitions, which can be observed at -0.016 V and 0.316 V (vs Ag|AgCl), respectively. Nevertheless, these values were slightly higher than those reported by Petit & Plichon (1998), which were found to be at -0.175 V and 0.205 V (vs Ag|AgCl) (Petit & Plichon, 1998). This positive potential peak shift is mainly due to the electrodeposition solution being in basic medium (Khalil et al., 2016). Furthermore, the deposition of iridium oxide nanoparticles on the Au substrate is believed to occur via the process of electro-flocculation in alkaline conditions (pH 13), as previously reported in the literature (Khalil et al., 2016; Nakagawa et al., 2009). It is suggested that electro-flocculation occurs due to the reduction of local pH at the electrode surface as the result of the production of protons from water oxidation, which could destabilize the colloidal nanoparticles in bulk solutions.

The thickness of the iridium oxide nanoparticles deposited on the surface of the Au substrate could also be qualitatively estimated by investigating the cathodic peak area (Kakooei et al., 2013). Figure 2a shows that increasing the number of deposition cycles increases the thickness of the iridium oxide nanoparticle thin film. In addition, the obtained cyclic voltammogram also becomes less symmetrical, as more iridium oxide nanoparticles are deposited on the substrate. Similar behavior has also been reported in other studies (Hu et al., 2009; Marzouk et al., 1998).

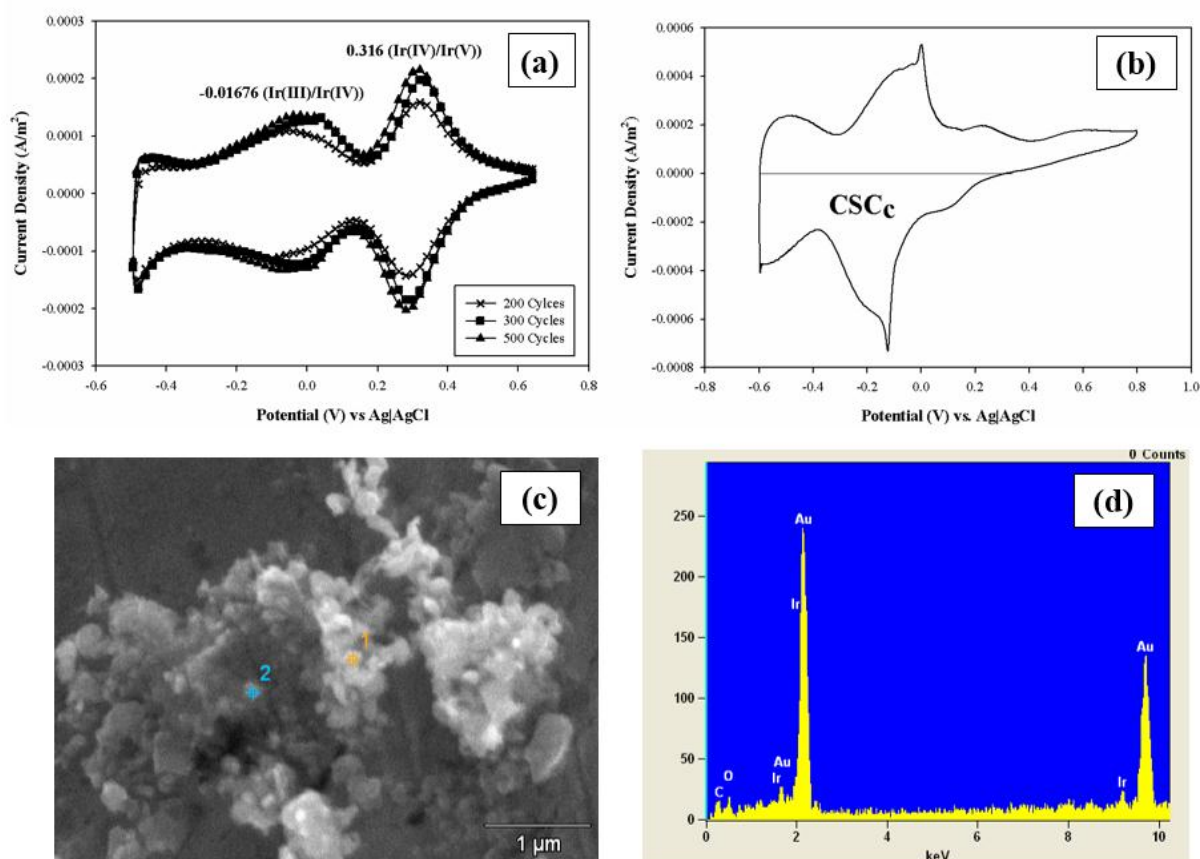


Figure 2 (a) Cyclic voltammogram of the electrodeposition of iridium oxide nanoparticles on the Au substrate; (b) CSC_c of the as-prepared electrode in PBS pH 7.2; (c) SEM image of the iridium oxide nanoparticles deposited on the Au substrate; (d) EDS spectrum of the electrode surface

It has also been reported that the iridium oxide nanoparticle thickness deposited in the metal substrate can be determined by measuring electrode cathodic charge storage capacity (CSC_c) (Kakooei et al., 2013; Mayer et al., 2001). Figure 2b presents the voltammograms of the as-prepared Au-based electrode deposited with iridium oxide nanoparticles for CSC_c determination in a PBS solution at pH 7.2. Based on the calculation, it was found that the CSC_c of the electrode was 0.201 mC/m². This value was significantly larger than that reported by Kakooei et al. for their stainless steel-based electrode (0.00104 mC/m²), indicating that our nanoparticle film thickness was significantly greater (Kakooei et al., 2013). Furthermore, the SEM image (Figure 2c) shows that the surface morphology of the electrode had rough features, as a result of nanoparticle aggregation during the electro-flocculation process (Nakagawa et al., 2009; Zhao et al., 2011b). In addition, the EDS spectrum (Figure 2d) provides additional evidence that iridium oxide nanoparticles had been successfully deposited onto the surface of the Au substrate.

3.3. Sensing Performance

The potentiometric responses of the as-prepared electrode were evaluated in pH buffer solutions of between pH 1.68 to 12.36 to investigate their sensing performance. Figure 3a shows the potentiometric response of the electrodes in a series of pH buffer solutions. Based on the results, it is clear that the electrode showed an excellent pH sensing ability and exhibited a super-Nernstian feature with a pH sensitivity of -73.7 mV/pH unit (R square = 0.9998). Previous studies have suggested that the pH responses of iridium oxide-based electrodes depend on electrode preparation methods, precursor materials, and its substrate. For instance, a

Nernstian response with a pH sensing response of around -59 mV/pH unit will be obtained when the electrode is prepared via thermal oxidation or sputtering (Yao et al., 2001; Huang et al., 2011). Yu et al. reported that an iridium oxide-based chemical sensor prepared by the thermal method exhibited a near-Nernstian response, with a pH response value of -59.7 mV/pH unit (Yu et al., 2015). However, when the electrode is prepared by electrochemical approaches, a super-Nernstian response will be obtained (Martinez et al., 2009; Kakooei et al., 2013; Khalil et al., 2016). In our previous report, a super-Nernstian electrode with pH sensitivity of -72.6 mV/pH unit was fabricated using a similar electrodeposition of iridium oxide nanoparticles on stainless steel substrate (Khalil et al., 2016). In another study, similar results were also reported by Kakooei et al., that electrodeposition of iridium oxide onto stainless steel will result in a super-Nernstian response in the range of -69.9 to -74.5 mV/pH unit (Kakooei et al., 2013). It is believed that this super-Nernstian feature is obtained mainly due to the formation of hydrated iridium oxides layers, such as $\text{IrO}_2 \cdot 4\text{H}_2\text{O}$, $\text{Ir}(\text{OH})_4 \cdot 2\text{H}_2\text{O}$ and $\{\text{IrO}_2(\text{OH})_2 \cdot 2\text{H}_2\text{O}\}^{2-} \cdot 2\text{H}^+$, on the surface of the metal substrate during the electrodeposition process (Olthuis et al., 1990; Martinez et al., 2009; Kakooei et al., 2013). Furthermore, Figure 3b shows the dynamic response time of the as-prepared electrode at various pH values. Based on the observation, it is clear that the as-prepared electrode exhibited a very good reversibility in pH measurement ability and the potential responses were independent of pH value and direction of pH change. Furthermore, no potential hysteresis was observed, even when the measurement was conducted cyclically in large steps between pH 1.68 to pH 12.36.

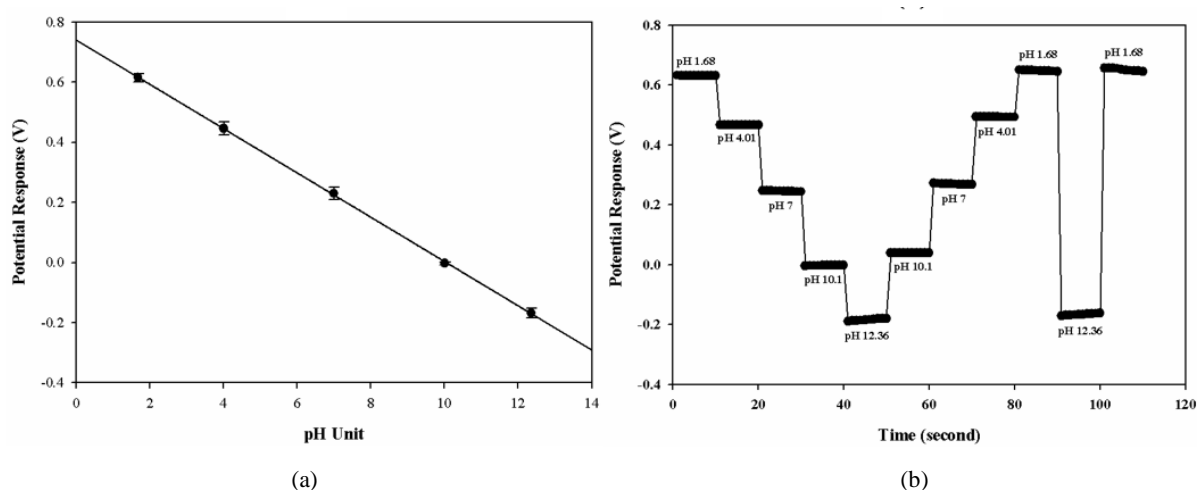


Figure 3 (a) Potentiometric responses of the electrodes in a series of pH buffer solutions; (b) dynamic response time of electrodes as a function of response time to pH changes

In addition, a series of pH measurements was carried out to validate the performance and sensing ability of the as-prepared electrode. Table 2 presents the results of the pH measurement of various sample solutions at different pH levels, using the as-prepared electrode and a commercial pH meter with a conventional glass electrode. Based on the results, it is apparent that the as-prepared electrode showed an excellent pH sensing ability and high accuracy with the commercial pH meter in a wide range of pH units. This suggests that the as-prepared super-Nernstian electrode fabricated via electrodeposition of iridium oxide nanoparticles on Au substrate could potentially be used as an alternative to the conventional glass electrode.

Table 1 pH measurement of sample solutions using a commercial pH meter and iridium oxide nanoparticle-based super-Nernstian electrode

Entry	pH		Accuracy
	Iridium Oxide Electrode	pH meter	
Solution 1	3.14	3.35	93.7 %
Solution 2	6.47	6.52	99.2 %
Solution 3	12.50	12.21	97.6 %
Solution 4	12.93	13.12	98.6 %

4. CONCLUSION

A potentiometric pH-sensing electrode with excellent sensing ability has been successfully fabricated by electrodeposition of iridium oxide nanoparticles onto the surface of Au wire. Monodisperse iridium oxide nanoparticles with a mean particle size of about 1–2 nm were synthesized via alkaline hydrolysis and used as the electrodeposition solution in cyclic voltammetry. Based on the results, a thin layer of hydrated iridium oxide nanoparticles was formed during the electrodeposition by the electro-flocculation process, creating rough features on the surface of the Au wire. The as-prepared electrode exhibited super-Nernstian behavior, with pH sensitivity of -73.7 mV/pH unit. The results also show that the as-prepared electrode exhibited very good pH sensing performance and could potentially be used as an alternative to the conventional glass electrode in commercial pH meters.

5. ACKNOWLEDGEMENT

We gratefully acknowledge the support of the US Department of Energy through the National Energy Technology Laboratory (DE-FE0009878). This paper is also supported by *Hibah Publikasi Internasional Terindeks untuk Tugas Akhir Mahasiswa (PITTA)* Universitas Indonesia (2287/UN2.R3.1/HKP.05.00/2018).

6. REFERENCES

- Charchour, N., Deslouis, C., Messaoudi, B., Pailleret, A., 2011. pH Sensing in Aqueous Solution using a MnO₂ Thin Film Electrodeposited on a Glassy Carbon Electrode. *Electrochimica Acta*, Volume 56(27), pp. 9746–9755
- Chen, Y., Taylor, P.L., Schersona, D., 2009. Electrochemical and in Situ Optical Studies of Supported Iridium Oxide Films in Aqueous Solutions. *Journal of the Electrochemical Society*, Volume 156(1), pp. F14–F21
- Elsen, H.A., Monson, C.F., Majda, M., 2009. Effects of Electrodeposition Conditions and Protocols on the Properties of Iridium Oxide pH Sensor Electrodes. *Journal of the Electrochemical Society*, Volume 156(1), pp. F1–F6
- Ges, I.A., Ivanov, B.L., Wedich, A.A., Baudenbacher, F.J., 2007. Differential pH Measurements of Metabolic Cellular Activity in NI Culture Volumes using Microfabricated Iridium Oxide Electrodes. *Biosensors and Bioelectronics*, Volume 22(7), pp. 1303–1310
- Glab, S., Hulanicki, A., Edwall, G., Ingman, F., 1989. Metal-metal Oxide and Metal Oxide Electrodes as pH Sensors. *Critical Reviews in Analytical Chemistry*, Volume 21(1), pp. 29–47
- Hashimoto, T., Miwa, M., Nasu, H., Ishihara, A., Nishio, Y., 2016. pH Sensors using 3D-block Metal Oxide-Coated Stainless Steel Electrodes. *Electrochimica Acta*, Volume 220, pp. 699–704

- Hashimoto, T., Yoko, T., 1995. Third-order Nonlinear Optical Properties of Sol-gel-derived V_2O_5 , Nb_2O_5 , and Ta_2O_5 Thin Films. *Applied Optics*, Volume 34(16), pp. 2941–2948
- Hu, J., Abdelsalam, M., Bartlett, P., Cole, R., Sugawara, Y., Baumberg, J., Mahajan, S., Denuault, G., 2009. Electrodeposition of Highly Ordered Macroporous Iridium through Self-assembled Colloidal Templates. *Journal of Materials Chemistry*, Volume 19(23), pp. 3855–3858
- Huang, W.D., Cao, H., Deb, S., Chiao, M., Chiao, J.C., 2011. A Flexible pH Sensor based on the Iridium Oxide Sensing Film. *Sensors and Actuators A: Physical*, Volume 169(1), pp. 1–11
- Huang, X., Ren, Q., Yuan, X., Wen, W., Chen, W., Zhan, D., 2014. Iridium Oxide based Coaxial pH Ultramicroelectrode. *Electrochemistry Communications*, Volume 40, pp. 35–37
- Johnson, M.D., Kao, O.E., Kipke, D.R., 2007. Spatiotemporal pH Dynamics Following Insertion of Neural Microelectrode Arrays. *Journal of Neuroscience Methods*, Volume 160(2), pp. 276–287
- Kakooei, S., Ismail, M.C., Wahjoedi, B.A., 2013. Electrochemical Study of Iridium Oxide Coating on Stainless Steel Substrate. *International Journal of Electrochemical Science*, Volume 8(3), pp. 3290–3301
- Khalil, M., Wang, S., Yu, J., Lee, R.L., Liu, N., 2016. Electrodeposition of Iridium Oxide Nanoparticles for pH Sensing Electrodes. *Journal of Electrochemical Society*, Volume 163(9), pp. B485–B490
- Kim, T.Y., Yang, S., 2014. Fabrication Method and Characterization of Electrodeposited and Heat-treated Iridium Oxide Films for pH Sensing. *Sensors and Actuators B: Chemical*, Volume 196, pp. 31–38
- Loon, G.V., Page, J.A., 1966. The Chemistry of Iridium in Basic Aqueous Solution: a Polarographic Study. *Canadian Journal of Chemistry*, Volume 44(4), pp. 515–520
- Manjakkal, L., Cvejic, K., Kulawik, J., Zaraska, K., Szwagierczak, D., Stojanovic, G., 2015. Sensing Mechanism of RuO_2 - SnO_2 Thick Film and LTCC Technologies. *Talanta*. Volume 147, pp. 233–240
- Martinez, C.C.M., Madrid, R.E., Felice, C.J., 2009. A pH Sensor based on a Stainless Steel Electrode Electrodeposited with Iridium Oxide. *IEEE Transaction on Education*, Volume 52(1), pp. 133–136
- Marzouk, S.A.M., Ufer, S., Buck, R.P., Johnson, T.A., Dunlap, L.A., Caselo, W.E., 1998. Electrodeposition Iridium Oxide pH Electrode for Measurement of Extracellular Myocardial Acidosis during Acute Ischemia. *Analytical Chemistry*, Volume 70(23), pp. 5054–5061
- Mayer, R.D., Cogan, S.F., Nguyen, T.H., Rauh, R.D., 2001. Electrodeposited Iridium Oxide for Neural Stimulation and Recording Electrode. *IEEE Transactions on Neural Systems and Rehabilitation Engineering*, Volume 9(1), pp. 2–11
- Nakagawa, T., Beasley, C.A., Murray, R.W., 2009. Efficient Electro-oxidation of Water Near its Reversible Potential by a Mesoporous IrO_x Nanoparticles Film. *The Journal of Physical Chemistry C*, Volume 113(30), pp. 12958–12961
- Nguyen, C.M., Rao, S., Yang, X., Dubey, S., Mays, J., Cao, H., Chiao, J.C., 2015. Sol-gel Deposition of Iridium Oxide for Biomedical Micro-devices. *Sensor*, Volume 15, pp. 4212–4228
- Olthuis, W., Robben, M.A.M., Bergveld, P., Bos, M., van der Linder, W.E., 1990. pH Sensor Properties of Electrochemically Grown Iridium Oxide. *Sensors and Actuators B: Chemical*, Volume 2(4), pp. 247–256
- Petit, M.A., Plichon, V., 1998. Anodic Electrodeposition of Iridium Oxide Films. *Journal of Electroanalytical Chemistry*, Volume 444(2), pp. 247–252

- Qingwen, L., Guon, L., Youqin, S., 2000. Response of Nanosized Cobalt Oxide Electrodes as pH Sensors. *Analytica Chimica Acta*, Volume 409(1–2), pp. 137–142
- Subasri, R., Malathi, R., Jyothirmayi, A., Hebalkar, N.Y., 2012. Synthesis and Characterization of CuO-hybrid Silica Nanocomposite Coatings on SS 304. *Ceramics International*, Volume 38(7), pp. 5731–5740
- Wang, M., Yao, S., Madou, M., 2002. A long-term Stable Iridium Oxide pH Electrode. *Sensors and Actuators B: Chemical*, Volume 81(2–3), pp. 313–315
- Xu, H.B., Lu, Y.H., Li, C.H., Hu, J.Z., 2010. A novel IrO₂ Electrode with Iridium-titanium Oxide Interlayers from a Mixture of TiN Nanoparticle and H₂IrCl₆ Solution. *Journal of Applied Electrochemistry*, Volume 40(4), pp. 719–727
- Xu, H., Liu, W., Cao, L., Su, G., Duan, R., 2014. Preparation of Porous TiO₂/ZnO Composite Film and its Phtocathodic Protection Properties for 304 Stainless Steel. *Applied Surface Science*, Volume 301, pp. 508–514
- Yao, S., Wang, M., 2002. Electrochemical Sensor for Dissolved Carbon Dioxide Measurement. *Journal of the Electrochemical Society*, Volume 149(1), pp. H28–H32
- Yao, S., Wang, M., Madou, M., 2001. A pH Electrode based on Melt-oxidized Iridium Oxide. *Journal of the Electrochemical Society*, Volume 148(4), pp. H29–H36
- Yu, J., Khalil, M., Liu, N., Lee, R., 2015. Iridium Oxide-based Chemical Sensor for In Situ pH Measurement of Oilfield-produced Water under Subsurface Conditions. *Ionics*, Volume 21(3), pp. 855–861
- Zhao, Y., Hernandez-Pagan, E.A., Vargas-Barbosa, N.M., Dysart, J.L., Mallouk, T.E., 2011a. A High Yield Synthesis of Ligand-free Iridium Oxide Nanoparticles with High Electrocatalytic Activity. *Journal of Physical Chemistry Letters*, Volume 2(5), pp. 402–406
- Zhao, Y., Vargas-Barbosa, N.M., Hernandez-Pagan, E.A., Mallouk, T.E., 2011b. Anodic Deposition of Colloidal Iridium Oxide Thin Film from Hexahydroxyiridate(IV) Solution. *Small*, Volume 7(14), pp. 2087–2093