**IOSR Journal of Engineering (IOSRJEN)** **www.iosrjen.org**
ISSN (e): 2250-3021, ISSN (p): 2278-8719
Vol. 05, Issue 05 (May. 2015), ||V2|| PP 14-22

# Polyaniline-coated electrodes for detection of dissolved oxygen levels in solution

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***Abstract:*** Emeraldine Base Polyaniline (EB-PANI), Emeraldine Salt Polyaniline (ES-PANI) and Leuco Emeraldine Base Polyaniline (LEB-PANI) were studied for detection of different dissolved oxygen levels in solutions. Optical properties of the polyaniline forms were characterized by Ultraviolet-Visible (UV-Vis) spectroscopy. To identify oxygen sensitivity of the PANI films, cyclic voltametry (CV) measurements were performed with the PANI films drop-casted on working platinum electrodes. Electrolyte solution in the CV measurements was based on phosphate buffer with salinity of 20‰ and pH 7.3. Pure nitrogen and oxygen gases were used to change oxygen levels that were monitored by a commercial dissolved oxygen probe. CV measurements showed the variations of current in corresponding to different oxygen concentrations. The correlation of the current and dissolved oxygen levels was also determined. The results exhibited the possibility of using LEB-PANI as sensing electrodes for detection of low concentrations of dissolved oxygen in aquaculture farming.

***Keywords:*** *cyclic voltametry, dissolved oxygen detection, leucoemeraldine base polyaniline, oxidation doping, polyaniline*

## I. INTRODUCTION

Dissolved oxygen (DO) concentration in water is one of the most important parameters of water for aquaculture farming, hence it is needed to be continuously monitored and controlled. DO measurement is used to identify amount of oxygen dissolved in a solution. Adequate DO concentration in water indicates good quality of water for aquaculture farming. When DO concentration is lower than 5 mg/l, aquacultural life is in danger. Large amount of fish might be fatal if DO concentration reaches 1-2 mg/l for several hours.

Commercial DO probes have been in market with various types from different manufacturers. Most DO sensors employ sensing technologies including optical based method which is commonly referred to as luminescent and the Clark electrochemical or membrane-covered electrode [1]. Hemera, Sacomam, Thethys Instruments, YSI supply DO sensors working based on optical method. Amount of oxygen is proportional to luminescence intensity of chemical dyes. Horiba, Greenspan Analytical, In-situ, Eutech-Thermo Scientific use polarographic electrodes and electrochemical advanced technologies. However, high cost of these sensors has hampered the application of these sensor systems in small and medium shrimp/fish farms. Therefore, the need of compact DO sensor development with low cost, simple operation has been increasing and has attracted the interest of many scientists in this field.

The optical method was used to measure DO levels in micro-scale water flows with an oxygen quenchable luminophore platinum (II) octaethyporphrin bound with thin polystyrene film [2]. Another work also used the optical method to measure DO concentrations within cell culture media by analyzing fluorescence intensity of dextran and ruthenium complex immobilized on poly(ethylene glycol) diacrylate microarray [3]. However, the optical method with a complicated setup and result analysis is only suitable for measurement in laboratories and it is difficult to apply for practical applications in aquaculture farming. Besides, electrochemical technology has been widely used for DO sensor development [4-6]. Chou et al. [5] investigated gold/Nafion electrodes with $H_2SO_4$ acid as a supporting electrolyte for DO detection in water. The sensitivity of DO sensors was 38.4 µA/ppm and the lowest limit of DO was 3.8 ppm. Peng Wang and his co-workers [6] used a silicon microprobe including Nafion coating on three platinum electrodes to measure DO levels at 0% atm, 10.5% atm and 21% atm. The difference between two curves in linear sweep voltammetry in air-equilibrated DI water and oxygen depleted DI water was attributed to oxygen reduction. However, the aim of this research is to measure DO concentration in blood for biological and biomedical use; hence, DO concentrations were not high. Moreover, repeatability was not satisfactory and the calibration curves were not established.

Recently conductive polymers have been investigated for different types of sensors [7-15] but only few of them have been used for DO measurements. Tieman et al. [16] used ionically conductive polymer poly(dimethyldiallylammonium chloride) coated on graphite electrodes as working electrodes to measure DO.

The authors used Pt auxilary electrode and Ag/AgCl reference electrode. DO concentration was measured by reduction at potential of -0.40 V versus Ag/AgCl. The linearity of concentration was in the range of 1.4-9.3 ppm. In addition, polyaniline (PANI) was once investigated for DO measurement [17]. A platinum electrode coated with PANI was examined as a potentiometric sensor. This PANI-coated electrode gave approximately 97 mV/decade of the oxygen concentration and a voltage signal of about 400 mV. A detection limit of DO was estimated of about 5 x $10^{-7}$ mol/l. The proposed mechanism based on the oxidation of reduced form (leucoemeraldine base PANI) leading to conversion into conducting salt PANI in the presence of oxygen bubbling in $H_2SO_4$ solution. In this research, pH of the medium was kept lower than 7 by a mixture of $H_2SO_4$ and NaOH. The oxidative doping due to existing $H_2SO_4$ 1 M solution could have caused conversion into conducting salt PANI. Therefore, the proposed mechanism of oxidation by oxygen bubbling is still not clear.

In this report three forms of PANI including Emeraldine Base Polyaniline (EB-PANI), Emeraldine Salt Polyaniline (ES-PANI) and Leuco Emeraldine Base Polyaniline (LEB-PANI) (**Fig. 1**) were investigated as sensing materials for detection of DO levels in solution. UV-Vis spectroscopy and cyclic voltametry (CV) were used to evaluate the DO sensitivity of these polymers. The increases in current of the CV measurements in corresponding to different DO concentrations were observed. The results showed possibility of using PANI-coated electrodes for DO sensors.

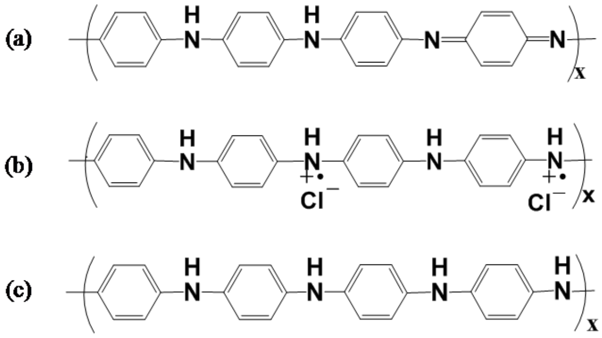

**Figure 1.** (a) Structure of EB-PANI. (b) ES-PANI. (c) LEB-PANI.

## II. EXPERIMENTAL

### 2.1. Materials

Emeraldine Base Polyaniline (EB-PANI) (99.7%, Mw 20,000), dimethyl sulfoxide (DMSO) (99.9%), phenylhydrazine (PHZ) (97%) were bought from Sigma Aldrich and hydrochloric acid (HCl) (37%) was bought from Merck. Disodium hydrogen phosphates dodecahydrate ($Na_2HPO_4.12H_2O$), sodium dihydrogen phosphate dihydrate ($NaH_2PO_4.2H_2O$) and sodium chloride (NaCl) were used to prepare testing solutions. All the chemicals were used as purchased without further purification. Oxygen ($O_2$) gas (99.999%) was supplied by Singapore Oxygen Air Liquide Pte. Ltd.

### 2.2. Preparation of polymer solutions

2.2.1. EB-PANI solution

Mix 30 mg of EB-PANI with 2.7 ml DMSO, stirring for 24 hours with a magnetic stirrer at room temperature to obtain EB-PANI solution. The solution was then filtered through a filter paper. The obtained polymer solution had dark blue color.

2.2.2. ES-PANI solution

EB-PANI powder was protonated by HCl 0.1 M solution to obtain ES-PANI (green color). The salt was filtered and rinsed by DI water to remove residual acid. Then ES-PANI was dried under vacuum at 60°C in a vacuum oven. 30 mg ES-PANI was dispersed in 2.7 ml DMSO to obtain ES-PANI solution. This solution underwent ultrasonification and centrifugal mixing.

2.2.3. LEB-PANI solution

ES-PANI was mixed with PHZ 97% to obtain LEB-PANI. Then the powder was rinsed in DI water, acetone and methanol to remove residual PHZ and dried at 60°C in the vacuum oven. After that LEB-PANI was dissolved in DMSO and this solution underwent ultrasonification and centrifugal mixing.

### 2.3. Fabrication of electrochemical chips

Electrochemical chips included one working electrode and one counter electrode (dimension of 3 mm x 9 mm) put separately with a distance of 3 mm. Both electrodes were made of platinum (Pt). Pt layers were sputtered with Univex 350 (Leybold, Germany) and patterned on silicon (Si) wafers coated with 700 nm thick $SiO_2$ by photolithography and lift-off techniques. The Pt electrodes had a thickness of 190 nm with a titanium adhesion layer.

4 µl of the PANI solutions was drop-casted on the working electrode of the electrochemical chips and these chips were heated in vacuum oven at 60°C for 24 hours to remove completely DMSO.

### 2.4. Characterization

UV-Vis absorption spectroscopy of the PANI samples was obtained from a double beam spectrophotometer Cary 100 (Varian, USA) in the wavelength range from 200 to 800 nm. To check oxygen sensitivity of the PANI forms, the quartz cuvettes containing the PANI solutions were bubbled with 0.5 psi of oxygen gas in 1-5 minutes. After each time of oxygen bubbling, UV-Vis spectra were recorded and compared. The variation of the UV-Vis spectra in the presence of oxygen (if any) can be applied for optical DO sensors using PANI layers as a color indicator.

The thickness of the Pt electrodes and the polymer films after fabrication was measured by a stylus profiler Dektak 6M (Veeco, USA).

### 2.5. Cyclic voltametry (CV) measurements

Testing electrolyte solutions were prepared from phosphate buffer which was made from 6 g $Na_2HPO_4.12H_2O$, 0.5 g $NaH_2PO_4.2H_2O$ and DI water to obtain 200 ml testing solution with pH 7.3. Then 4 g NaCl was added to make the solution have salinity of 20‰. The testing solution was prepared to imitate the conditions of water in shrimp ponds.

The testing solutions were bubbled with nitrogen ($N_2$) gas for 15 minutes to minimize DO concentration in the solution, approximately 1.5 ppm. Then oxygen ($O_2$) gas was bubbled through the solution with a pressure of 1 psi for 15-90 seconds to create various DO concentrations in the solutions. DO concentrations were measured by a commercial DO probe DO6400TC/T (Sensorex, US) with a measurement range of 0-20 mg/l, 0.01 mg/l resolution and ±1.5% accuracy.

The polymer coated chips were dipped in the testing solutions in which the polymer part was immersed completely. CV measurements were performed with a potentiostat/galvanostat PGSTAT 302N (Metrohm, Autolab, the Netherlands) and a silver/silver chloride (Ag/AgCl) reference electrode RE-6 (Basi Inc., US). The polymer chips were mounted on two crocodile clips (**Fig. 2**). The current was set from 10 µA to 10 mA, the scanning rate was 50 mV/sec, the temperature was about 28 °C ± 1 °C.

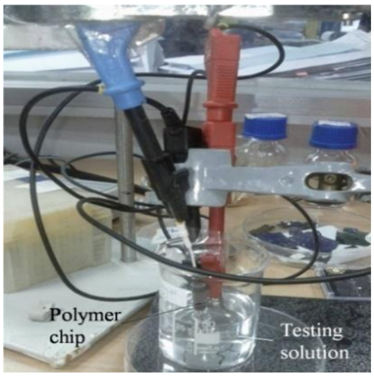

**Figure 2.** The polymer chip mounted on two crocodile clips.

## III. RESULTS AND DISCUSSION

### 3.1. UV-Vis spectroscopy of EB-PANI, ES-PANI and LEB-PANI

UV-Vis spectroscopy of EB-PANI, ES-PANI and LEB-PANI was carried out with Cary 100 (Varian, USA) in the wavelength range from 200 to 800 nm. UV-Vis absorption spectra of EB-PANI, ES-PANI and LEB-PANI in DMSO are shown in **Fig. 3**.

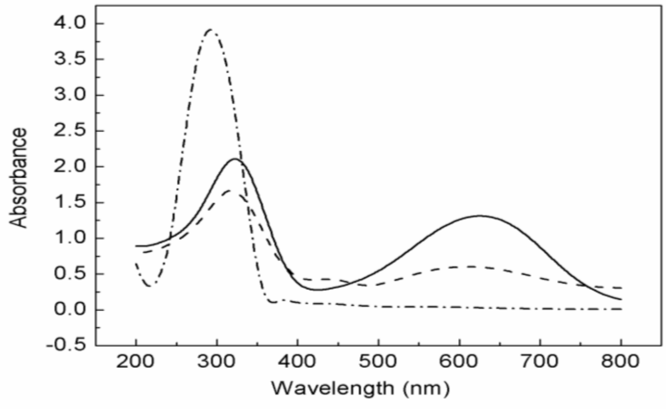

**Figure 3.** UV-Vis absorption spectra of EB-PANI (solid line), ES-PANI (dash line) and LEB-PANI (dash dot line) in DMSO.

UV-Vis spectrum of EB-PANI in DMSO solvent shows two peaks at wavelength of 324 nm and 625 nm. This result is in good agreement with literature values [18-20]. The absorption peak at 324 nm is assigned to the $\pi$ - $\pi^*$ transition of the benzenoid rings. The peak at 625 nm originates from the exciton transition of the quinoid rings [19]. The absorption spectrum of HCl-doped PANI in DMSO solvent showes peaks at 289 nm, 456 nm and 663 nm. The two bands have been assigned to the optical absorption of the polaron band [18, 20]. The absorption spectrum of LEB-PANI has only one peak at 292 nm, which is in good agreement with the published value [21].

The UV-Vis spectra of PANI solutions with and without pure oxygen bubbling were recorded. The quartz cuvettes containing the polymer solutions were bubbled with pure oxygen for 1-5 minutes. After each duration of oxygen bubbling, UV-Vis spectra were recorded and compared (*see Supplementary Materials for the UV-Vis spectra of the PANI forms with oxygen bubbling*). The UV-Vis spectra of EB-PANI, ES-PANI and LEB-PANI solutions almost did not change as the oxygen gas was bubbled into the solutions. However, the UV-Vis spectra of LEB-PANI solutions which included residual PHZ showed an increasing peak at 450 nm with an increase in DO concentration (*Figure S4 of Supplementary Materials*). The color of LEB-PANI changed from transparent to green when oxygen was bubbled into the solution. It was found that the color change was due to oxidation of the residual PHZ in the LEB-PANI preparation (*Figure S5 of Supplementary Materials*).

### 3.2. Platinum electrodes

Series of the electrochemical chips with Pt electrodes were fabricated by photolithography, sputtering and lift-off processes. **Fig. 4** shows the fabricated Pt electrodes and a diced chip coated with the PANI film on the working electrode. The thickness of the PANI films varied from 500 nm to several micrometers.

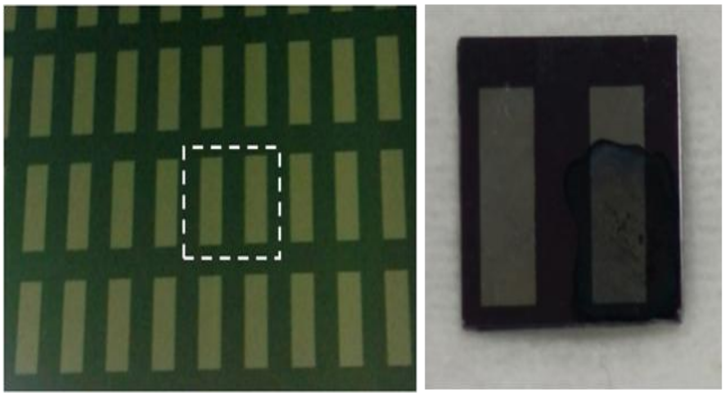

**Figure 4.** The platinum electrodes on a silicon wafer before dicing into seperate chips (left) and the diced chip coated with the PANI film on the working electrode (right).

### 3.3. CV measurements of the PANI-coated chips

CV measurements were performed with the PANI-coated platinum electrode as the working electrode, another Pt counter electrode and the Ag/AgCl reference electrode. For each CV measurement, at least two chips of the same batch were measured to check reproducibility. The potential was scanned with various ranges and it was found that the stable potential range of the fabricated electrodes was from -0.6 V to +1.1 V. Various DO concentrations in the testing solutions were created by bubbling $N_2$ for 15 minutes and $O_2$ for 15-90 seconds. In this study, high DO concentrations were used to check the DO sensitivity of the PANI forms. Basing on the measurement of the commercial DO probe, 1 minute of oxygen bubbling could create 16.05 mg/l of DO concentration in the testing solutions. Due to the limited measurement range of the commercial DO probe (i.e. 20 mg/l), the DO concentrations created by durations of oxygen bubbling larger than 1 minute were estimated correspondingly.

#### 3.3.1. EB-PANI coated chips

**Fig. 5** shows cyclic voltammograms of the EB-PANI coated chips immersed in the testing solutions which were bubbled with $N_2$ and $O_2$ for 15, 30, 60 and 90 seconds (DO concentrations ranged from 1.50 ppm to 26.00 ppm).

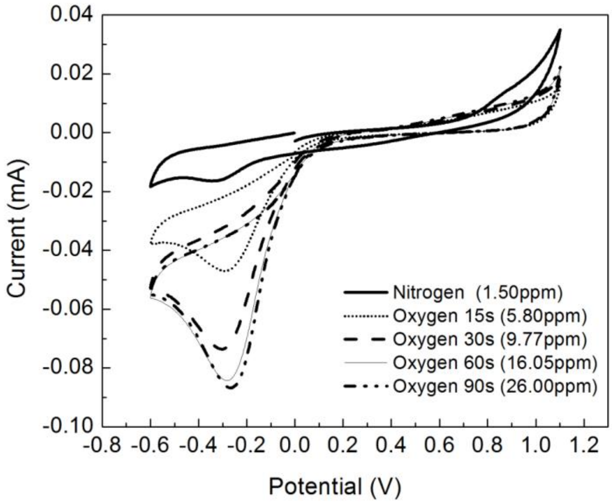

**Figure 5.** CV plots of the EB-PANI chips with $N_2$ purging (bold solid line), $O_2$ bubbling for 15 seconds (dot line), 30 seconds (dash line), 60 seconds (solid line), 90 seconds (dash dot dot line).

When DO concentration in the solution increases, the magnitude of current increases with DO concentrations from 0.015 mA to 0.085 mA at the cathode peak of -0.3 V. There is large difference in current when DO concentration increases from 1.5 ppm (corresponding to $N_2$ purging) to 26 ppm (90 seconds of $O_2$ bubbling). The increase in current exhibits the DO sensitivity of the EB-PANI films. The change in current corresponding to estimated DO concentration is 2.86 µA per 1 ppm of DO concentration. This sensitivity is however lower than the published sensitivity of 38.4 µA/ppm [5] and 12.5 µA.cm$^{-2}$/ppm [16]. This difference in sensitivity is due to different electrode materials and different sizes of electrodes.

The relationship between the cathode current at -0.3 V and DO concentrations was shown in **Fig. 6**. The increase in current of the EB-PANI thin films follows an exponential Decay function. It was observed that the current increased steeply from 1.5 ppm to 10 ppm DO. Beyond 16 ppm DO, the current did not change much and it became stable. It could be attributed to the saturation of DO in the testing solution with 90 seconds of oxygen bubbling. Therefore after this measurement, the duration of oxygen bubbling was limited not more than 90 seconds.

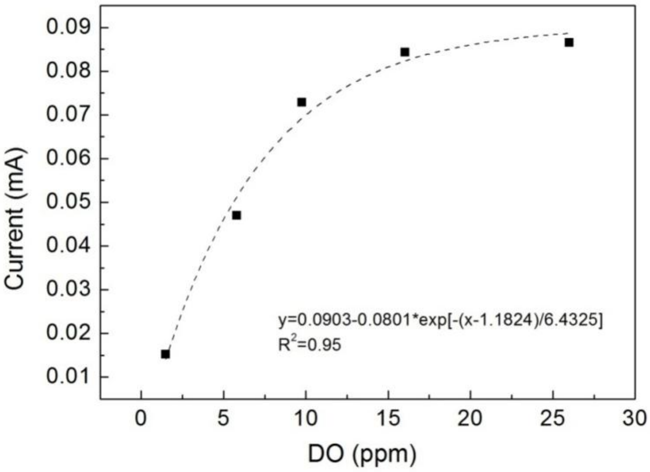

**Figure 6.** The relationship between the cathode current and DO concentrations at -0.3 V of the EB-PANI coated chip.

3.3.2. ES-PANI coated chips

Cyclic voltammograms of the ES-PANI coated chips which were bubbled with $N_2$ and $O_2$ for 15, 30, 60 and 90 seconds (DO concentrations ranged from 1.50 ppm to 26.00 ppm) are shown in **Fig. 7**.

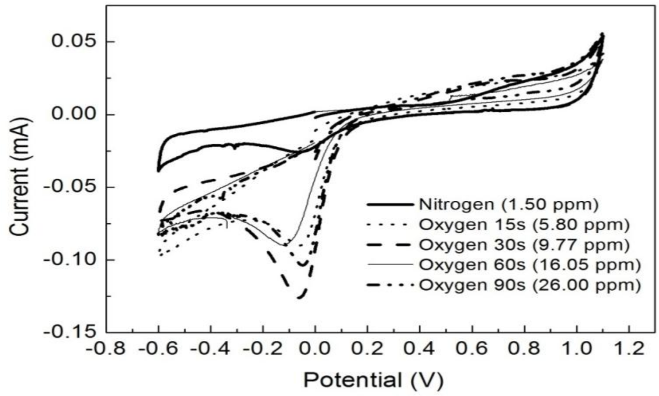

**Figure 7.** CV plots of the ES-PANI chips with $N_2$ purging (bold solid line), $O_2$ bubbling for 15 seconds (dot line), 30 seconds (dash line), 60 seconds (solid line), 90 seconds (dash dot dot line).

When DO concentration in the solution increases from 1.5 ppm to 9.77 ppm, the magnitude of current increases with DO concentrations from 0.026 mA to 0.125 mA at the cathode peak of -0.05 V. In comparison with the EB-PANI chips, the cathode peak is found to shift to -0.05 V. The change in current of the ES-PANI chips is much larger (11.97 µA/ppm of DO concentration) in the range of 1.5-9.77 ppm DO. However, the current decreases when DO concentration increases to 16.05 ppm (corresponding to 60 seconds of oxygen bubbling). Two ES-PANI chips of the same measurement gave the same results. The instable increase of the current can be attributed to the scratched ES-PANI film after the CV measurements (*Figure S6 of Supplementary Materials*). It should be noted that the ES-PANI layer was not durable. The layer was stripped off gradually after the CV scans from 1.5 ppm to 26 ppm DO and was removed completely after two times of CV scans. The stripping of the ES-PANI layer can be due to dispersion of the conductive ES-PANI particles which were charged under an electrical field in the electrolyte solution.

### 3.3.3. LEB-PANI coated chips

**Fig. 8** shows the cyclic voltammograms of the LEB-PANI coated chips exposed to oxygen bubbling for 15, 30, 60 and 90 seconds. Similar to the ES-PANI chips, the cathode peak of the LEB-PANI is -0.05 V. This peak is similar to the reduction peak of -0.03 V of LEB-PANI in CV measurements at pH 1 of Edward Song et al. [22].

This potential indicated the reduction of LEB-PANI film at the cathode. Large increase in magnitude of the current is also observed when DO concentrations increased from 1.5 ppm (corresponding to $N_2$ purging) to 26 ppm (1.5 minutes of oxygen bubbling). The current increases with DO concentrations from 0.018 mA to 0.1 mA at -0.05 V. **Fig. 9** shows the relationship between the cathode current at -0.05 V and DO concentrations. The increase in current of the LEB-PANI thin films also follows an exponential Decay function similar to the EB-PANI films. The current of the LEB-PANI films increases steeply from 1.5 ppm to 10 ppm DO and does not change much after 15 ppm DO. The change in current corresponding to estimated DO concentration is 3.35 µA per 1 ppm of DO concentration. The results showed that the DO sensitivity of the LEB-PANI coated chips is higher than the EB-PANI form.

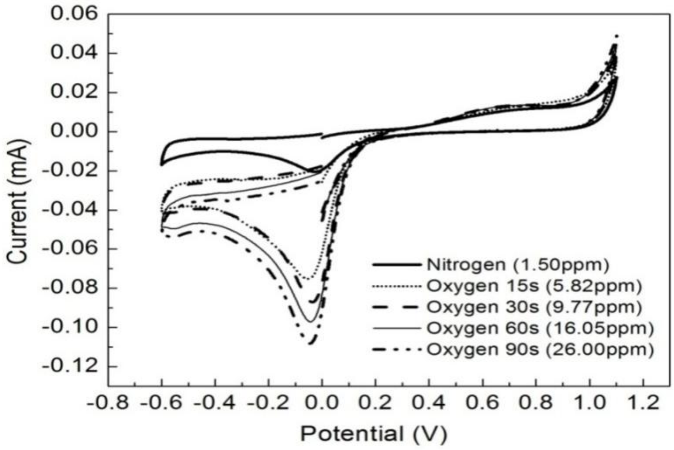

**Figure 8.** CV plots of the LEB-PANI chips with $N_2$ purging (bold solid line), $O_2$ bubbling for 15 seconds (dot line), 30 seconds (dash line), 60 seconds (solid line), 90 seconds (dash dot dot line).

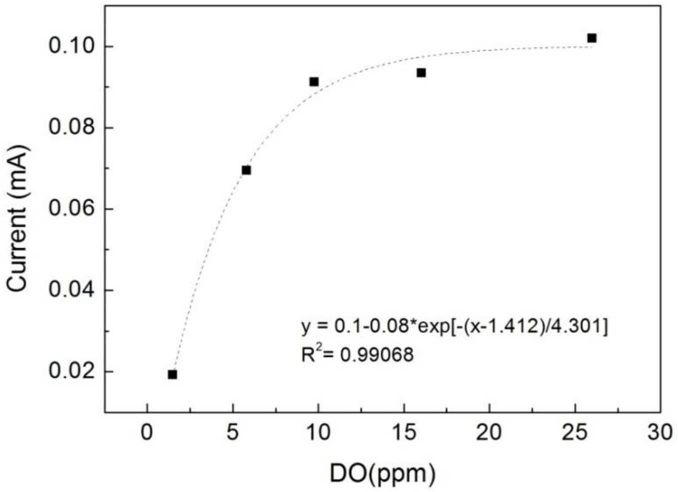

**Figure 9.** The relationship between the cathode current and DO concentrations at -0.05 V of the LEB-PANI coated chip.

3.3.4. Stability of the PANI electrodes

To check reversibility and consistency of the current increase between nitrogen and oxygen bubbling, the CV measurements of the PANI chips were performed when the chipswere exposed to bubbling nitrogen (15 minutes) and oxygen (30 seconds) for two times. CV plots after two times of oxygen bubbling (9.77 ppm DO) are almost the same (*Figure S7 of Supplementary Materials*). Therefore, the PANI electrode chips have good reversibility.

To check stability of the PANI electrodes, the CV measurements of the PANI electrodes were performed as long as the CV plots could be obtained. DO concentration varied from 1.50 ppm to 26.00 ppm for the CV measurements of each chip. The EB-PANI electrodes could be measured for 5 weeks and the LEB-PANI layers could be measured for 7 weeks whereas the ES-PANI electrodes could only be measured for 1-2 weeks. The increase of the cathode current and DO concentrations of the EB-PANI and LEB-PANI electrodes in 5 and 7 weeks plotted from the CV scans also follows an exponential Decay function (*Figure S8 and Figure S9 of Supplementary Materials*). The variations in the current of the EB-PANI and LEB-PANI chips were observed. The current signal of the EB-PANI chips was stable for 2 weeks and decreased in the following weeks. For the LEB-PANI chips, although there was large fluctuation at high DO concentrations, the current was somehow stable at below 10 ppm DO after 7 weeks.

3.3.5. Possible sensing mechanism

The cathode reaction relating to the redox reaction of oxygen in solution with the PANI films coated on the Pt electrode is shown in the following reactions (1) and (2). For simplicity, a general sign is used in the reaction (1), in which PANI represents different forms of PANI and $[\mathrm{PANI}]^{n-}$ represents the different electrochemical redox states of PANI which have been reported in many studies [23-25].

$$\mathrm{PANI} + n\,e \rightarrow [\mathrm{PANI}]^{n-} \qquad (1)$$

$$\mathrm{O_2} + 4\,e \rightarrow 2\,\mathrm{O^{2-}} \qquad (2)$$

Depending on the form of PANI (EB-PANI, ES-PANI or LEB-PANI) the difference in the consumed number of electrons causes the different cathodic potentials (as observed in the CV measurements). The cathodic potential of EB-PANI is more polarized than that of LEB-PANI. This leads to the fact that the oxygen reduction with the LEB-PANI electrode is easier than with the EB-PANI and the higher DO sensitivity of the LEB-PANI coated chips.

In the reaction (1), the PANI film receives electrons to transform into a charge state $[\mathrm{PANI}]^{n-}$ and a part of charge is transferred to oxygen to cause the reaction (2). The CV plots of the PANI forms show only one cathode peak. It could be implied that the reduction reaction is followed by one-step reaction. The reduced oxygen $\mathrm{O^{2-}}$ may be combined with $[\mathrm{PANI}]^{n-}$ to produce a new compound like $[\mathrm{PANI\text{-}O_2}]$ (**Fig. 10**). The same structure of $[\mathrm{PANI\text{-}O_2}]$ was also proposed by D. V. Zhuzhel'skii [26].

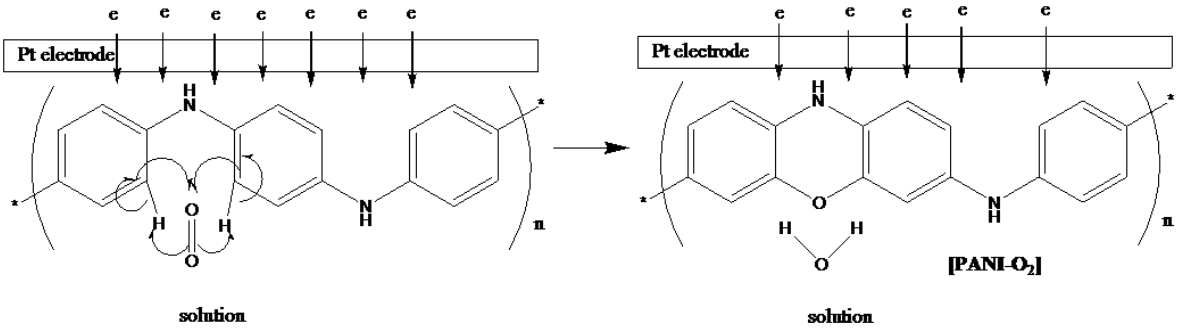

**Figure 10.** Mechanism of reduced oxygen at the PANI-coated Pt electrode.

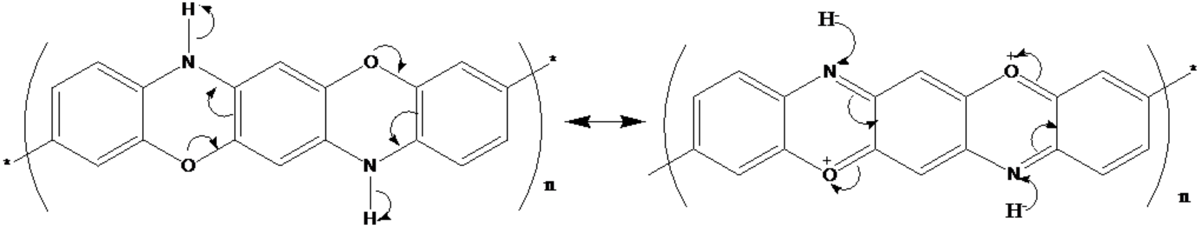

**Figure 11.** Resonance in [PANI-$O_2$] structure to form oxoniumcations.

In the presence of DO in solution, two oxygen atoms approach the PANI films and attach to the benzene rings of the PANI. The resonance in the structure then occurs and oxonium ions are generated (**Fig. 11**). When there are more oxygen molecules, more oxonium ions are formed and the conductivity of the PANI films increases. The increase in oxygen concentration leads to the increase in current intensity. However, oxygen present in the solution can react at some extent. When all the reaction sites for oxygen are occupied, the current does not increase much as DO concentration increases. This leads to the observed saturation of the increase in the current (**Fig. 6** and **Fig. 9**).

## IV. CONCLUSIONS

In this study we have investigated the DO sensitivity of the EB-PANI, ES-PANI and LEB-PANI films. The UV-Vis spectra of the PANI solutions did not show any change in the presence of dissolved oxygen. However, the CV measurements of the EB-PANI, ES-PANI and LEB-PANI films coated on the Pt electrodes showed the increase in current as DO concentration in the solutions increased. The steep current increase of the PANI films in the DO range of 1.5-10 ppm is suitable for monitoring of water quality in aquaculture farming. The correlation of the current and DO concentrations was studied for the EB-PANI and LEB-PANI electrodes. The higher DO sensitivity (3.35 µA/ppm) and higher stability of the LEB-PANI films enables the feasibility of using LEB-PANI films as sensing materials in DO sensors.

## V. ACKNOWLEDGMENTS

The authors highly appreciate the financial support of Vietnam National University - Ho Chi Minh City for this study through the grant number B2013-76-04.

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