

# 9,10-ANTHRAQUINONE-2,6-DISULFONIC ACID DISODIUM SALT/ EPOXY GRAPHITE COMPOSITE FOR ANODE IN MICROBIAL FUEL CELL

## Article history

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Mimi Hani Abu Bakar<sup>a,b,c\*</sup>, Neil F Pasco<sup>b</sup>, Ravi Gooneratne<sup>c</sup>, Kim Byung Hong<sup>b</sup>

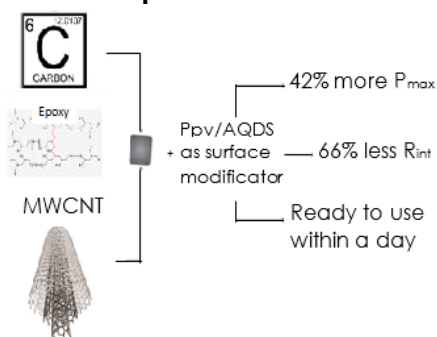
\*Corresponding author  
mimihani@ukm.edu.my

<sup>a</sup>Fuel Cell Institute, Universiti Kebangsaan Malaysia (UKM), Bangi, Selangor, Malaysia

<sup>b</sup>Lincoln Agritech Ltd, Lincoln, Christchurch, New Zealand

<sup>c</sup>Lincoln University, Lincoln, New Zealand

## Graphical abstract



## Abstract

Properties such as electrical conductivity, low resistivity, chemicals and corrosion resistance are mostly found in carbon based materials. Epoxy resin is excellent for electrical insulation and can be used as a conductor with the addition of conductive filler. Combinations of carbon and epoxy show qualities of a conductive electrode, mechanically strong with design flexibility and thus makes them suitable as electrodes in microbial fuel cell (MFC). In this study, graphite-epoxy composites were fabricated with multi-walled carbon nanotube (MWCNT) embedded in the matrix surface. 9,10-Anthraquinone-2,6-disulfonic acid disodium salt/polypyrrole (PPy/AQDS) was used as mediator, covalently electrografted on electrode's surface. Electrochemical stability of anodes during continuous operation were measured in air-cathode MFCs. It appears that maximum power in MFC could be increased up to 42% with surface modification using PPy/AQDS. Internal resistance ( $R_{int}$ ) could be reduced up to 66% with the inclusion of MWCNT. These findings show that a one-day fabrication of a ready-to-use conductive electrode is possible for graphite content between 70-80% (w/w).

**Keywords:** Anode, disodium salt of Anthraquinone disulfonic acid /polypyrrole, graphite-epoxy composite, microbial fuel cell

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## 1.0 INTRODUCTION

In general, an electrode should have qualities such as good electrical conductivity, low resistivity, stable against chemicals and corrosion [1]. These features are mostly found in carbon based materials, such as graphite, thus making it popular material for electrodes [2]. Carbon with biological catalysts in many aspects also conforms to requirements of a biosensor, thus making it acceptable material for electrode fabrication in a microbial fuel cell (MFC). Epoxy resins on the other hand are polymers with good electrical insulation properties [3], which is valuable in

the electronics industry. This trait however is adjustable to conductor or semiconductor with the addition of conductive filler [4]. Therefore, a combination of carbon as filler and epoxy resin offers fabrication of a polymer composite, which are conductive [5], effortless in processing as well as moulding, and corrosion resistance [6, 7].

Studies conducted on carbon-epoxy composite within the field of fuel cell and biology shows its favourable applications in bipolar plates of proton exchange membrane fuel cell (PEMFC) and biosensor. In the area of bipolar plates, Du and Jana (2007) found that their fabricated carbon-epoxy with

the total filler loading greater than 50 wt% showed good conductivity, mechanical integrity and chemical stability at temperature above 150 °C and at pH 4, much suitable for PEMFC application [5]. Llopis *et al.* (2005) showed that their amperometric glucose biosensor worked more efficiently when a mixture of glucose oxidase (GOD) powder, epoxy resin, graphite powder and tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ) were applied at a ratio (wt%) of 5:76:9.5:9.5 for automated detection of glucose [8]. Kirgoz *et al.* (2006) discovered that combination of the composite biosensor with a thin layer solution of *Pseudomonas putida* cells modified the surface could give minimum detection limit on phenol almost 1,000 times lower than thick film microbial biosensor and conventional oxygen electrode [7]. Later, Ocaña *et al.* (2014) found that aptamer when immobilized on the surface of graphite-epoxy composite gave good detection range for cytochrome c and high sensitivity, which is suitable for an aptasensor [9]. Pumera *et al.* (2006) learnt that carbon nanotube-epoxy composite exceeded in both electrochemical and mechanical

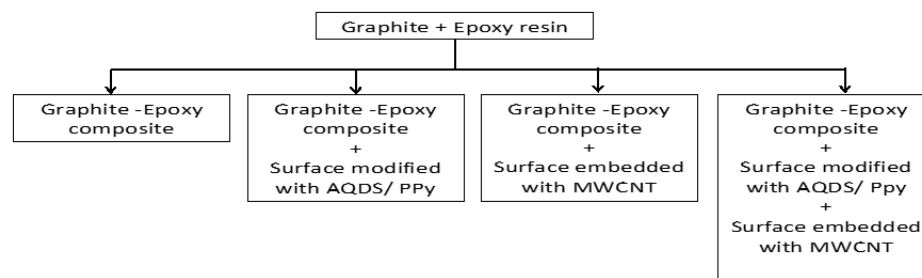
Anthraquinone-2,6-disulfonic acid disodium salt/polypyrrole (AQDS/ PPy) was used here as external mediator. It was electrochemically grafted to the composites' surfaces to induce preferred orientation on the active site and increased the electron transfer rates [12, 13]. Performance of the graphite-epoxy composites in terms of electrochemical stability as anodes during continuous operation were measured in air-cathode MFCs. For this purpose, characterization of the MFC systems were measured through the polarization and power density analyses.

This study was designed to analyse the graphite-epoxy composite with more than 50% graphite contents, fabricated in a day using simple technique, on its capability when operated as anode in air-cathode MFCs' environment. In addition to that, the effect of embedded MWCNT in composite matrix and its compatibility with AQDS/ PPy electropolymerised on its surface were also assessed through the MFC performance.

## 2.0 METHODOLOGY



(a)



(b)

**Figure 1** Cyclone shape MFC (a) and the fabricated graphite-epoxy electrodes (b) used in this study

qualities when compared to graphite-epoxy composite for sensor application [10]. Based on Ma *et al.* (2010) and Vahedi *et al.* (2010), carbon nanotubes as filler in the epoxy system had the ability to improve conduction pathway in the epoxy matrix and increased conductivity at loading as low as 0.5 wt. % [6, 11]. These qualities; strong mechanical properties in bipolar plates and good conductivity as biosensors, gave the indication that the graphite-epoxy composite has the potential to be applied in an MFC application. Unfortunately, it is not known whether there had been studies done more than seven days on the performance of the graphite-epoxy composite as electrodes in MFC. In addition to that, the composite ease of shapes gives more opportunities to flexibility in reactor and electrode designs for MFC performance study.

In this study, graphite-epoxy composites were fabricated with multi-walled carbon nanotube (MWCNT) embedded in the matrix surface. 9,10-

### 2.1 Inoculation

Working buffer was a 50 mM phosphate buffer solution (PBS) containing  $\text{NH}_4\text{Cl}$  (0.31 g/L),  $\text{NaH}_2\text{PO}_4 \cdot 2\text{H}_2\text{O}$  (3.12 g/L),  $\text{Na}_2\text{HPO}_4$  (4.58 g/L), and  $\text{KCl}$  (0.13 g/L) at pH 7 used for preparing acetate media and for analysis [14, 15]. Basal media of 7 mM acetate containing  $\text{CH}_3\text{COONa}$  (1 g/L), peptone of casein (1 g/L) and yeast extract (2 g/L) was dissolved in PBS [16]. The media was autoclaved at 121 °C for 15 min prior to use. Analytical solution were made using Milli-Q water from EASYpure UV unless otherwise stated. All MFCs were inoculated with effluent from an existing MFC acetate batch fed operated for approximately two years, at 28 °C with an external resistor of 500  $\Omega$ .

### 2.2 Anode Construction

The base for the anodes were made from graphite powder mixed with epoxy resin in four different ratios

by adjusting the weight of the graphite powder (% w/w): 53 (total weight of 430 g), 73 (total weight of 730 g), 78 (total weight of 930 g) and 84 (total weight of 1,250 g). The total filler loading was more than 50 wt% to get desired low inherent resistance of fabricated electrodes. Ratio between the resin (norSKI® part A) and its hardener (norSKI® part B) followed Pumera *et al.* (2006) at (w/w) of 20:3 [10]. The combined material was manually blend using spatula until the texture turned flaky and packed into the PCR tubes ( $\varnothing$  0.4 cm) at the length of 1.5 cm.

For the embedding of MWCNT into the matrix of graphite epoxy composite, only two ratios of graphite powder were used (% w/w): 73 and 78. This was because graphite powder ratio of 53% (w/w) required longer curing hours while graphite powder ratio of 84% (w/w) could not produce detectable redox peaks when analysed using cyclic voltammetry (CV). MWCNT was prepared through mixing of 1 mg of MWCNT with a 0.4 mL N,N-Dimethylformamide (DMF) in a vibrator for one min. The mixture was later topped up with 0.6 mL of 70% ethanol and sonicated in water bath for five minute. Loading of the MWCNT ink into the base of graphite-epoxy composite was done at different ratios of MWCNT (% w/w): 0.04 and 0.06. The MWCNT mixtures were manually blend using spatula and dried under room temperature until the texture became muddy dry. The mixture paste was topped up about 0.3 cm high on the packed graphite- epoxy resin mixture in the PCR tube, to become the electrode's surface.

Prior to the surface modification methods, each of the packed PCR tubes was centrifuged at 14,000 g for 1.5 min to compress and remove remaining air in the paste. A copper wire was inserted at the bottom of each tube for electrical contact. The filled PCR tubes were then cured at 80 °C for 12 h. They were then allowed to cool at ambient temperature for 30 min. Later, each excess PCR tube wall was cut until the wall was at the same level with the surface of the fabricated graphite-epoxy composite electrodes. The electrode surface area was polished, first on a wet fine emery paper (Norton, P400), then rinsed with Milli-Q water and dried on paper towel before polished on white paper until mirror like surface appeared.

### 2.3 Electrografting with 9,10-Anthraquinone-2,6-Disulfonic Acid Disodium Salt (AQDS)/ Polypyrrole (PPy)

Polypyrrole (PPy) was purified before used [17, 18]. PPy was chosen in this study because of its high electronic conductivity and relatively long period of stability [19] to provide good support for AQDS. PPy was passed to a column of alumina about 4 cm in height stuffed in a glass pipette. Surface modification of AQDS was done using method described in Feng *et al.* (2010) [20]. Here, 4 mM PPy was added to 4 mM AQDS in 70% ethanol and 120 mM hydrochloric acid (HCl) [19, 20]. The mixture was mixed under nitrogen environment for 5 minutes prior to the electropolymerization. Surface

of the electrodes were then modified through electropolymerization in a three-electrode configuration electrochemical cell, free from mixing, yet still under nitrogen environment. An Autolab potentiostat was used to control the constant potential of +1,100 mV applied to the anode for about 1 h ( $t_{\text{Quiet}} = 5$  s,  $t_{1\text{st step}} = 1$  s and  $t_{2\text{nd step}} = 1$  s). The freshly prepared AQDS/ PPy- modified electrode was first rinsed with 100 mM HCl and water before thoroughly rinsed in 100 mM PBS.

### 2.4 Single Chamber Air-Cathode Microbial Fuel Cell

Four cyclones shaped MFCs with anode compartment capacity of 25 mL were constructed from a 50 mL Falcon tube ( $\varnothing$  3 cm) (Figure 1a). Tube wall of 3.5 cm x 2.4 cm was cut and glued with cation exchange membrane (Ultrax) from BASF Fuel Cell Inc. (Somerset, NJ, USA) while its opposite wall was cut at 1.4 cm x 1.4 cm and glued with butynol Dunlop sheet with one small hole punctured for working electrode. The Falcon tube cap was used to cover the cyclone MFC and was equipped with three holes: a small square about 1 cm x 1 cm for reference electrode (Ag/ AgCl) during the working electrode potential poisoning and electrochemical analysis, and one small circle of  $\varnothing$  0.15 cm for incoming gas. An air-cathode from a 10% Pt-carbon cloth (Fuel Cell Earth LLC, Stoneham, MA) was fastened to the exterior wall of the Ultrax membrane with a nickel strip and insulated garden wires. The nickel strip acted as current collector at the cathode. The anode compartment was kept anoxic through continuous gassing with oxygen-free nitrogen. The working electrode was the fabricated graphite -epoxy composite electrodes of  $\varnothing$  0.4 cm (Figure 1b). The graphite -epoxy composite electrodes were placed almost 90° facing the Ultrax membrane interior wall at a constant distance of about 1-2 mm.

### 2.5 Operation

Inoculation method was adapted and adjusted from the method in Watson and Logan (2011), who studied the effect of AQDS/ PPy on carbon felt in dual chambered MFC [21]. Here, about 50% of each 12 new MFCs were filled with anolyte and topped up with acetate media. The anolyte came from a two year old acetate fed MFC, where its early culture originated from aerobic trickling filter. The electrodes were then connected with a 1,000  $\Omega$  resistor.

### 2.6 Analyses

Cell voltage ( $E$ , mV) across the external resistor were measured every six times daily using a four channel Quadstat 164 potentiostat (eDAQ Pty Ltd, NSW, Australia) with continuous recording using an e-corder 1621 (eDAQ Pty Ltd, NSW, Australia) data acquisition system. Current ( $I$ , mA) and power ( $P$ , mW) were calculated using the Ohm's law,  $I = E/R_{\text{ext}}$ , where  $R_{\text{ext}}$  is

the applied external resistance. The current density (mA/cm<sup>2</sup>) and power density (I E/ Anode area, mW/ m<sup>2</sup>) are normalized by the projected area of the anode.

Cyclic voltammetry (CV) was measured using a BASi epsilon C3 cell stand with potentiostat (BASi, Indiana, US). A three-electrode system was used, comprising a coiled platinum wire as auxiliary electrode, an Ag/AgCl electrode as reference electrode and the fabricated anodes as working electrode. The scan rate applied was 20 mV/s between -250 to +500 mV in 50 mM ferricyanide/ ferrocyanide. The experiment was performed at room temperature in a Faraday's cage.

Polarization curve and the power density curves were produced by using anode potential poisoning method, adapted from linear sweep voltammetry method of Lanas and Logan (2013) [22]. In this study, anode became the working electrode and cathode as the counter and reference electrode. The polarization curves were obtained starting with open circuit voltage (OCV) with each potential changed in decreasing order after every pseudo steady-state achieved, or not more than 20 min intervals (whichever comes first) over a complete fed batch cycle. Analysis was conducted once the voltage output was stabilized after replenishing the media.

### 3.0 RESULTS AND DISCUSSION

#### 3.1 Fabrication of Graphite-Epoxy Composite Anodes

The inherent resistances measured for the fabricated graphite-epoxy composites in this study were also compared to the  $\varnothing$  3 mm commercial graphite rod and a 20% (w/w) graphite-epoxy composite fabricated by Corb *et al.* (2007), which was fabricated using a hot press machine at 80 °C for 40 min (Table 1) [2].

**Table 1** Inherent resistance measured for graphite-epoxy composite anodes

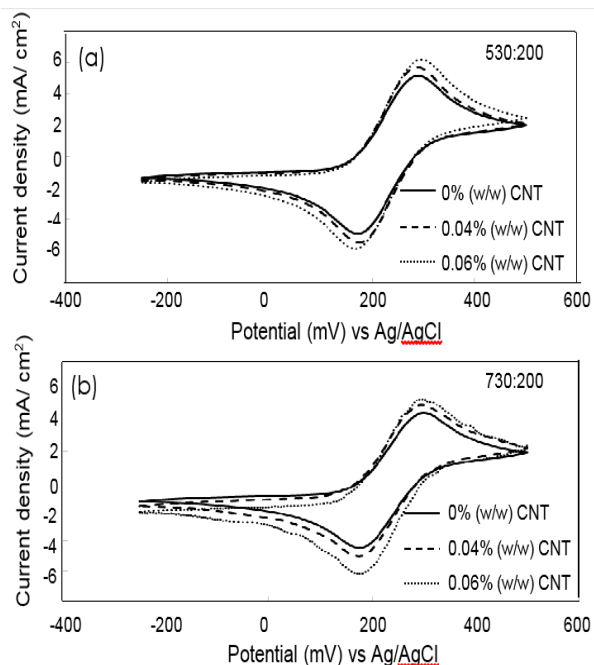
Graphite % (w/w)	Inherent Resistance ( $\Omega$ )		
	% MWCNT (w/w)		
	0	0.04	0.06
20*	7.3	not available	not available
53	34.0	not available	not available
73	6.1 $\pm$ 0.3	5.7 $\pm$ 0.4	5.8 $\pm$ 0.4
78	4.3 $\pm$ 0.3	4.0 $\pm$ 0.3	4.4 $\pm$ 0.5
84	4.6 $\pm$ 0.5	not available	not available
$\varnothing$ 3 mm commercial graphite rod	0.4 $\pm$ 0.0	not available	not available

\*Corb, I., F. Manea, C. Radovan, A. Pop, G. Burtica, P. Malchev, S. Picken, J. Schoonman [2] evaluated the inherent resistance at sample thickness of 1 mm over sample area of 81 mm<sup>2</sup>. All the fabricated electrodes in this study were evaluated at sample thickness of 1.5 cm over sample area of 12.6 mm<sup>2</sup>.

The commercial graphite rod by far having the least inherent resistance in this study most probably due to the fabrication technique applied by the industry, which also involves heating above 2,000 °C. Samples from 53% graphite had much higher resistance than the other graphite-epoxy composite samples in this study. At the same time, the curing time applied in this study proved not to be sufficient for 53% graphite where the surfaces were easily penetrated from the prodding of the multimeter probes. The incomplete curing might have built the high inherent resistance for the 53% graphite. All the fabricated samples showed significant differences (t-Test, p>0.05) in inherent resistance from the commercial electrode, however showed comparable inherent resistance with the graphite-epoxy composite electrode consisting of 20% graphite [2]. Sandler *et al.* (1999) reported that the critical filler volume fraction for percolation, a conductive path created through three-dimensional network of conductive filler particles, is between 5 and 20 vol. % [23]. Llopis *et al.* (2005), Corb *et al.* (2005) and Ocaña *et al.* (2014) used a filler as low as 20% (w/w) to fabricate good graphite-epoxy composite biosensors that exhibited good conductivity [2, 8, 9]. However, to fabricate an epoxy composite with very low filler contents, either a long curing time period is required (more than two days) [8, 9] or require the help of expensive machinery, such as hot pressed machine [2].

O'Hare *et al.* (2002) however, had used filler contents ranging between 40 to 60% for their electrodes and cured them by degassing in vacuum oven [24]. They discovered that only the electrode with 60% filler gave voltammetric peaks response similar to the classic peaks shaped of a solid macroelectrode. By increasing the volume filler fraction to more than 60% (w/w) in this study, a graphite-epoxy composite was able to be fabricated in less than a day, without using expensive machinery and complex method, while at the same time able to show good conductive behaviour. Introduction of 0.04% MWCNT into the surface matrix had reduced the inherent resistance of the plain graphite-epoxy composite samples, although not significantly (t-Test, p>0.05) by 7% less for both 73 and 78% samples (Table 1). For samples with 84% graphite, the addition of 0.04% MWCNT into the surface matrix had turned the surface very dry and brittle. After increasing the concentration of MWCNT to 0.06%, the inherent resistance of each samples had increased to 2% for 73% graphite, 9% for 78% graphite and had caused very brittle surface for 84% graphite. The embedding of 0.04% MWCNT within composite matrix that consists of graphite more than 70%, was able to bring down the inherent resistance of the graphite-epoxy composite slightly. However, adding another 0.02% more had proven to give unfavourable effect through increasing the inherent resistance for the samples. Both samples from the 73 and 78% graphite might end up like the 84% graphite samples if more than 0.06% MWCNT added into its system. Though the MWCNT could contribute towards reinforcement of a MWCNT-

epoxy composite system [25], too much filler in an epoxy system will create non-homogeneity in dispersion, especially when using simple hand shearing as applied in this study. This may have a lesser effect on conductivity [25] but increases the possibility of mechanical failure. It was reported that the structural failure in one of the studies of MWCNT-epoxy composite system, was due to the addition of MWCNT from 0.05 to 0.5% (w/w) [6]. They explained that the increased in fillers will prevent the movement of polymer chains from the epoxy causing the system to become brittle. The amount of low loading however, is dependent on epoxy system, aggregation mechanism and the type of filler applied [26]. In this study, the MWCNT was added into an epoxy mixture that already had graphite as its filler. Therefore the reason of too much filler might have led to the surface failure of 84% graphite samples.



**Figure 2** Cyclic voltammograms between different MWCNT loadings in graphite-epoxy composite anodes at scan rate 20 mV/s and in 50 mM ferricyanide/ferrocyanide electrolyte at room temperature (n=3)  
 $E_{1/2}$  for:

73% (w/w) graphite (530:200)	78% (w/w) graphite (730:200)
(a):	(b):
No CNT= $231 \pm 0.3$	No CNT= $239 \pm 2.0$
0.04% (w/w) CNT = $236 \pm 0.3$	0.04% (w/w) CNT = $236 \pm 1.2$
0.06% (w/w) CNT = $231 \pm 0.2$	0.06% (w/w) CNT = $236 \pm 4.6$

The ability of the fabricated epoxy composite electrodes to deliver current response from the reaction of electrolyte can be measured through CV. The redox potential of the ferricyanide/ferrocyanide calculated from the half waves,  $E_{1/2}$  obtained from the plain graphite-epoxy composite electrodes shows astray from the standard reduction potential  $E^{\circ}$  of

ferricyanide/ferrocyanide. When the  $E^{\circ}$  of ferricyanide/ferrocyanide is +162 mV (vs Ag/AgCl) [27], the calculated  $E^{\circ}$  from the fabricated electrodes were: 73% graphite detected about 69 mV more while 78% and 84% graphite detected more than 72 mV (Figure 2). There was no significant difference (t-Test,  $p > 0.05$ ) for  $E_{1/2}$  detected between the 78% graphite samples and  $\varnothing$  3 mm commercial graphite ( $E_{1/2} = 234 \pm 0.3$ ), which was used for comparison.

This shows the likeness in current response ability between the 78% graphite samples to the  $\varnothing$  3 mm commercial graphite. However, there were significant differences (t-Test,  $p < 0.05$ ) when the  $E_{1/2}$  of the commercial graphite was being compared to both 73 and 84% graphite samples. No  $E_{1/2}$  was detected for electrodes with 53% graphite, which might be due to the incomplete curing. For 78% graphite samples, the addition of MWCNT on those two MWCNT loadings did not give significant difference (t-Test,  $p > 0.05$ ) in  $E_{1/2}$  when compared to its respective plain samples, between the two MWCNT loadings and the  $\varnothing$  3 mm commercial graphite. Meanwhile, for 73% graphite samples, the addition of 0.06% (w/w) MWCNT had given significant difference (t-Test,  $p < 0.05$ ) in  $E_{1/2}$  when compared to the 0.04% (w/w) MWCNT loading and the  $\varnothing$  3 mm commercial graphite. No  $E_{1/2}$  analysis was done to 84% graphite samples due to the surface failure after the incorporation of MWCNT into the surface matrix. From the  $E_{1/2}$  analysis, the 78% graphite samples show as if the addition of MWCNT into its system did not improve nor worsen the current response ability, unlike 73% graphite samples where 0.04% loading was able to improve its current detection. This could be due to the effect of the filler agglomerating during blending and curing, creating conductive network, which covers the nonconductive epoxy area [26]. Although the inherent resistance results show the  $\varnothing$  3 mm commercial graphite had the lowest resistance, the  $E_{1/2}$  performance of the fabricated graphite-epoxy composites (73 and 78% graphite contents) had showed to be comparable in current response to the  $\varnothing$  3 mm commercial graphite in this study albeit the inherent resistances.

For surface modification with PPy and AQDS, 78% graphite samples and MWCNT loading of 0.04% (w/w) were applied due to not much difference in current response between the two MWCNT loading as well as the low inherent resistance and consistent  $E_{1/2}$  showed by 78% graphite samples.

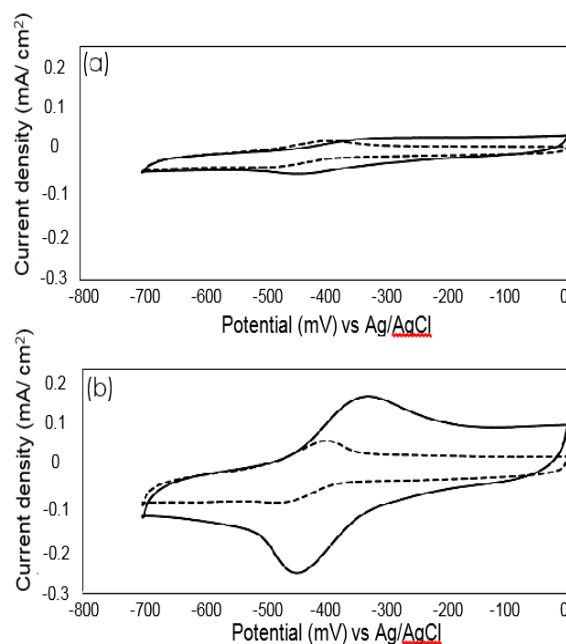
Figure 3 shows that the electrografting technique had successfully modified the electrode surfaces. For the embedded MWCNT with AQDS through the formation of redox potential, was seen at  $E_{1/2}$  close to  $E^{\circ}$  of AQDS, -395 mV (vs Ag/AgCl) [28]. This is promising for application as mediated anode in MFC, due to the  $E^{\circ}$  reported for  $\text{NAD}^+/\text{NADH}$  is -525 mV (vs A/AgCl) [29], which is lower than the surface modified electrodes. The results in this study agrees with Feng et al. (2010a), who had obtained  $E_{1/2}$  at -451 mV (vs Ag/AgCl) when using pretreated carbon felts as base for the electrodes [20]. Although the peaks

were not clear for the plain graphite-epoxy composite samples, there are evident current size and  $E_{1/2}$  differences between the initial modified electrodes and after 24 h rinsing in PB solution, where the current size and  $E_{1/2}$ , became smaller in current and slightly more negative in  $E_{1/2}$  potential. Feng *et al.* (2010a) also observed the difference in peaks size and clarity between two different materials, glass carbon and carbon felt, after their surface modified with AQDS/PPy [20]. They explained that curves with larger currents represented enhancement made by PPy/AQDS on the modified surfaces while good peak clarity denotes the low charging inherent current by the electrode. The shift of waves to negative potential in voltammetry analysis reflected the change in the equilibrium of the active redox couple as a function of the equilibrium constant,  $K_{eq} = [\text{OH}^-][\text{H}^+]/[\text{H}_2\text{O}]$ , and can be mathematically explained by the Nernst equation,  $E = E^{\circ'} - (RT/F) \cdot \ln([C]/K_{eq}[A])$  [30]. The  $R$  represents the gas constant of 8.3147 J/K mol,  $T$  represents the temperature,  $F$  represents the Faraday constant of 96,485 C/mol and  $[C]$  represents the reduced concentration of substrate  $[A]$  in mol/dm<sup>3</sup> when species  $A$  is in equilibrium with species  $B$  from  $A \rightleftharpoons B$ ,  $B + e \rightleftharpoons C$ . The rinsing had removed the excess modification from the electrode surface. This might have caused the electrode surface to become less acidic, subsequently reducing the  $K_{eq}$  and eventually pushing the wave towards negative potential.

### 3.2 Power Generation

The main aim of this study was to fabricate strong and easy-to-mould graphite-epoxy composites using simple methods described in the anode construction section. The prepared electrodes were used as anodes in MFC operations and the performance was measured through anodes polarization and power density on the 13<sup>th</sup> day after start up. The electrodes polarization results (Figure 4a & b) showed that between the fabricated anodes, open circuit potential (OCP) for anodes from MFC2 and MFC2m, gave lower OCP (more negative), -192 mV (vs. Ag/AgCl) less by 62% than MFC1 and MFC1m. The lower OCP observed from these anodes show the contribution of MWCNT in keeping down the anode potential regardless with or without the AQDS/PPy for surface modification. Low anode potential, as close to the  $E^{\circ}$  of NAD<sup>+</sup>/NADH is necessary to prevent the bacteria from gaining metabolic energy, thus reducing maximum attainable voltage for MFC [27]. These OCP for anodes however are 56% more shifted to the positive potential than  $E_{1/2}$  of surface modified graphite-epoxy with AQDS/PPy recorded in CV using 0.1 M PB, free from bacterial cell (Figure 3). This occurrence was also reported by Feng *et al.* (2010a) where the CV analysis showed that peak waves for their AQDS/PPy modified carbon felt as anodes in MFC were shifted towards the positive potentials when compared to the surrounding without bacterial cell [20]. Based on Logan (2008), bacteria regulate the concentration ratio of the reduced/oxidized species

to maximise the degradation of substrate through NAD<sup>+</sup>/NADH, and to transfer the electrons to the anode electrode through other terminal enzymes, which has different potentials [29].



**Figure 3** Cyclic voltammograms of AQDS/PPy surface modified on 78% graphite samples (a) without and (b) with 0.04% (w/w) MWCNT loading embedded in the surface of composite matrix before (—) and after 24 h rinsing (---) in 0.1 M PB electrolyte at room temperature. Scan rate used was 20 mV/s.  $E_{1/2}$  for:

Without MWCNT (a):	With MWCNT (b):
0 h rinsing = not available	0 h rinsing = $-389 \pm 0.6$
After 24 h rinsing = not available	After 24 h rinsing = $-438 \pm 0.9$

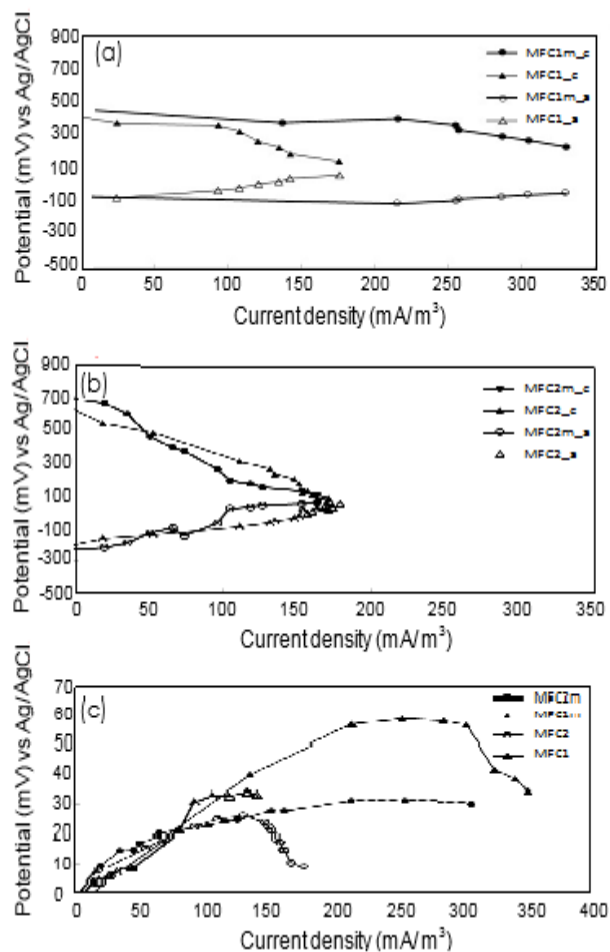
Therefore, it seems that the anode potential will vary according to the bacterial strain dominating the electrode and whether the electrode is with or without biofilm on it. The existence of MWCNT in the anode matrix however did not show any improvement (decreasing) in the overpotential. It gave a significant increase in anode potential, about 214.5 mV (from -164 to +50.5 mV). In fact, this is 38% higher than MFC1 to drive similar current densities from 0 to 176 mA/m<sup>2</sup>. With the introduction of AQDS/PPy for surface modification, a low overpotential of 24 mV (from -72 to -48 mV) was achieved by MFC1m, while the current densities were pushed further from 0 to 330 mA/m<sup>2</sup> (Figure 4a). The surface applied mediator acts as catalyst on the electrode and at the same time reduced the large overpotentials of the electrodes [20, 31]. For the cathode, the application of commercial Pt on carbon clothes were made consistent for each MFCs in this study, and the overpotential from cathode electrodes due to the

oxidation reduction reaction were much higher than the anode electrodes [32]. Therefore, the cathode electrodes with large overpotentials became the limiting factor, which indicates the domination on the cell voltage output [33]. It is necessary to get low overpotential since electrode overpotential in an MFC is a constitution of three basic losses, 1) activation due to energy lost during electron transfers, 2) bacterial metabolism through substrate oxidation, and 3) mass transport referring to flux of reactants and products during the reaction [29]. In addition to that, these high overpotentials are shown clearly in the power curves (Figure 4c). The MFC1m samples that had low anode electrode overpotentials, gave high maximum power density of 59 mW/ m<sup>2</sup> at the current density of 255 mA/ m<sup>2</sup>; and followed by MFC1 with 42% less, MFC2m with 47% less and MFC2 with 56% less in power density than MFC1m.

Apart from that, the power density curves also gives quick indication on internal resistance ( $R_{int}$ ) of the MFC system, where a power curve leaning more to the right will have lesser  $R_{int}$  than those with symmetrical curves [27].  $R_{int}$  of an MFC system could refer to resistance experienced by the electrons through the electrodes and interconnections, resistance experienced by the ions through the membranes, the ionic strength in the electrolytes and many more occurred within the MFC system. Using  $R_{int}$  calculation method from Logan (2009),  $R_{int} = P_{max}/ I^2$ , where  $P$  is maximum power generated and  $I$  is current obtained at  $P$  maximum [29], MFC1m and MFC2m samples showed  $R_{int} < 100$  k $\Omega$ , while MFC1 and MFC2 had  $R_{int} > 100$  k $\Omega$ .

This shows that the AQDS/ PPy surface modification had successfully bring down the  $R_{int}$  of plain graphite epoxy anodes by 48% and plain graphite epoxy anodes with embedded MWCNT by 66%. Further comparison of  $R_{int}$  between fabricated anode without surface modification shows that anode embedded with MWCNT had 22% lesser  $R_{int}$  than the anode samples without MWCNT. This shows the ability of graphite-epoxy composite with embedded MWCNT anodes to bring down the  $R_{int}$  in the MFC system.

The reason for the low maximum power generated by these embedded MWCNT anodes relative to the non-embedded MWCNT, however requires further investigation. The obtained maximum power is much lower in performance than reported, 1,303 mW/m<sup>2</sup> [20], where their surface modification technique of AQDS/ PPy on carbon felt was adopted onto this study's fabricated graphite-epoxy composite samples. Since the only similarity between this study and Feng *et al.* (2010a) is the surface modification technique [20], the inferior performance observed in my study could be due to the differences in the electrode material used, bacterial culture applied as the inoculum and the catholyte used in in MFC.



**Figure 4** Power generation for MFCs operated with (MFC<sub>y</sub>m,  $y = 1, 2$ ) and without (MFC<sub>y</sub>,  $y = 1, 2$ ) the AQDS/ PPy surface modified anodes on plain graphite-epoxy anodes and on anodes with embedded MWCNT (MFC2<sub>x</sub>,  $x = m, 0$ ) and without the embedded MWCNT (MFC1<sub>x</sub>,  $x = m, 0$ ). (a) Anode and cathode polarization curves when using plain graphite as base, (b) when using graphite-epoxy composite embedded with MWCNT as base, and (c) power density curves of four MFCs. Data presented in this figure are representative of at least three independent experiments.

Note:

c = cathode electrode, a = anode electrode and m = AQDS/ PPy surface modification

## 4.0 CONCLUSION

We have demonstrated that it is possible to prepare a ready to use electrode within one day from graphite-epoxy composite with more than 70% graphite using a simple and cheap technique, while showing similarity in current response close to the conductive commercial graphite rod. We have also shown that the fabricated electrodes are capable to be used as anodes in MFCs, while the  $P_{max}$  could be increased by 42% and  $R_{int}$  reduced by 48% through simple surface electrografting with AQDS/ PPy solution. Although

anode samples with embedded MWCNT were not superior in maximum power density compared to samples without MWCNT, the  $R_{int}$  however showed a reduction by up to 66% for the anode with PPY/AQDS surface modification. Further studies are required to determine whether the anode with embedded MWCNT will show a higher maximum power density if allowed to operate for a much longer duration.

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