Enhancement of Characteristics of Nitrogen-Doped Graphene Composite Materials Prepared by Ball Milling of Graphite with Melamine: Effect of Milling Speed and Material Ratios

(Penambahbaikan Ciri-Ciri Bahan Komposit Nitrogen Terdop Grafin Menggunakan Kaedah Penggilingan Bola Campuran Grafit dan Melamin: Kesan Kelajuan Penggilingan dan Nisbah Bahan)

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ABSTRACT

Nitrogen-doped graphene has been prepared using the ball milling method that is known to be eco-friendly, scalable and economic. The parameters studied in the synthesis were the mass ratio of starting materials (graphite and melamine) and speed of the ball milling. To determine its structure and properties, the nitrogen-doped graphene was characterized using Field Emission Scanning Electron Microscopy with Energy Dispersive X-Ray (FESEM-EDX), RAMAN Spectroscopy and X-Ray Diffraction (XRD). Based on FESEM-EDX analysis, the doped composite exhibited nitrogen content of ~3.5%. The nitrogen-doped graphene was examined as a replacement for platinum catalysts in fuel cells. Different composite catalysts were evaluated using a Rotating Disk Electrode (RDE) to test the Oxidation Reduction Reaction (ORR) performance. Based on ORR performance comparison, the composite with highest performance was then used to fabricate a Membrane Electrode Assembly (MEA). Testing on MEA performance was conducted on a Fuel Cell Station, where Open Circuit Voltage (V_{OC}) of 0.14 V was obtained. The results indicate that the ball milling method may produce an efficient nitrogen-doped graphene MEA electrode from graphite and melamine only. Compared with a platinum counterpart, the new composite material electrode showed soundly high current-potential characteristics and fuel conversion efficiency.

Keywords: Ball milling; fuel cells; membrane electrode assembly (MEA); oxidation reduction reaction (ORR); rotating disk electrode (RDE)

ABSTRAK

Tujuan kajian ini adalah untuk mensintesis nitrogen terdop grafin menggunakan kaedah penggilingan bola yang mesra alam, boleh diskala dan ekonomi. Parameter yang dikaji dalam proses sintesis ialah nisbah jisim bahan mentah (grafit dan melamin) dan kelajuan penggilingan bola. Untuk menentukan struktur dan sifat sampel, nitrogen terdop grafin telah dicirikan menggunakan alatan seperti FESEM-EDX, RAMAN Spectroscopy dan XRD. Berdasarkan keputusan analisis FESEM-EDX, komposit yang terdop nitrogen menunjukkan kandungan nitrogen sebanyak ~3.5%. Nitrogen terdop grafin dikaji sebagai pengganti kepada pemangkin platinum dalam sel bahan api. Komposit pemangkin yang berbeza dinilai menggunakan Cakera Elektrod Berputar (RDE) untuk menguji prestasi ORR. Berdasarkan keputusan perbandingan prestasi ORR, pemangkin yang terbaik akan digunakan untuk memfabrikasi Pemasangan Elektrod Membrane (MEA). Pemangkin ini juga menunjukkan bacaan voltan sebanyak 0.14 V (V_{OC}) semasa diuji di Stesen Sel Bahan Api. Keputusan menunjukkan kaedah penggilingan bola mungkin boleh menghasilkan elektrod nitrogen terdop grafin MEA yang efisien daripada grafit dan melamin sahaja. Berbanding dengan platinum, bahan komposit elektrod yang baru ini menunjukkan ciri-ciri arus elektrik yang tinggi dan kecekapan penukaran bahan api.

Kata kunci: Cakera elektrod berputar (RDE); pemasangan elektrod membran (MEA); penggilingan bola, sel bahan api; tindak balas pengurangan pengoksidaan (ORR)

INTRODUCTION

Sustainable energy and healthy environment are main concerns to humanity. Non-renewable (fossil fuel) energies are non-sustainable and have negative impact on the environment and society, as can be observed from greenhouse effects and climate changes. Fuel cells are one strategy to preserve the environment. However, the cost of platinum that is commonly used as a catalyst in the fuel cells adds to their manufacturing costs (Qu et al. 2010). For instance, the high platinum catalyst cost limits commercialization of Proton Exchange Membrane Fuel Cells (PEMFC) (Kurungot et al. 2016). Moreover, platinum

active sites and catalytic activities lead to the blocking and poisoning at the cathode in some fuels such as methanol (Girit et al. 2009). Finding newer catalysts with lower costs is thus imperative. Nitrogen-doped graphene has been reported to compete with platinum (He et al. 2005).

Currently, graphenes are highly demanded in global market production due to their wide industrial applications (Olson 2012). Allen et al. (2010) showed that graphite, a sustainable material, can be used in electrodes due to its high electrical and thermal conductivity, and ability to be used in graphene production. Graphene sheets exist inside graphite, at only one atom thickness scale. Graphene and graphite have resemblance in properties and functions, with the former having much higher electrical conductivity due to its quasiparticle nature. The quasiparticle nature in graphene is a dynamic property of the electrons, as stated by Suprun and Shmeleva (2017). Doping the graphene may further increase its electrical characteristics and replace platinum (Kurungot et al. 2016). Wu et al. (2011) showed that nitrogen-doped graphene exhibits higher energy storage performance than pristine graphene. According to Xue et al. (2015), nitrogen-doped graphene is useful in energy conservation and energy storage in fuel cell devices. Maddi et al. (2018) also stated that nitrogen doping affects diffusion of charge carriers in graphene.

Graphenes can be produced by various methods such as electrochemical exfoliation, mechanical exfoliation, arc-dischage method and Chemical Vapour Deposition (CVD) (Xu et al. 2018). A common method to produce high-quality graphenes is the peeling-off (so-called scotch tape) method (Novoselov et al. 2004). However, the scotch tape is inefficient as it produces a low yield of graphene. Graphene can further be produced from graphite by ball milling with relatively high production yield and low cost at large scale production (Shams et al. 2015).

Doping the graphene with nitrogen enhances its characteristics as stated previously. Ball milling has been followed using a nitrogen gas flow in closed reaction vessels. This method is difficult and costly. Using ball milling to produce graphene from graphite and melamine under simple working conditions has been described, and the composite was examined as supercapacitor electrode material (Xue et al. 2015).

Due to its simplicity, eco-friendliness, scalability and low cost, ball milling is the method of choice here to produce nitrogen-based composite material from graphite and melamine. The main goal of this study is to enhance the ball mill prepared nitrogen-doped graphene composite characteristics. The effect of the mass ratio of starting materials on composite characteristics is studied. The effect of ball milling speed on composite material characteristics is also studied. The nitrogen-doped graphene composite material is also assessed as a catalyst in fuel cells as a replacement for the costly platinum

system. All such studied are performed here for the first time to our knowledge.

The assumption is that milling speed and graphite to melamine ratio may influence the nitrogen content in graphene and thus affect its physical and electrical properties. The synthesized catalysts were characterized using FESEM, EDX, Raman Spectroscopy, and XRD to check the structure and properties of nitrogen-doped graphene. The synthesized catalysts were evaluated using a RDE to test the ORR performance. The activity of synthesized catalyst has been assessed based on ORR performances as described earlier (Kurungot et al. 2016). ORR performances were tested through Cyclic Voltammetry (CV) and Linear Sweep Voltammetry (LSV) analysis. The best catalyst, with highest ORR performance, was then fabricated on a MEA to test its performance at Fuel cell station. The composite material fuel conversion performance was then compared to a platinum electrode.

METHODS

STARTING AND COMMON MATERIALS

Graphite powder, melamine powder, 5% by mass of ethanol and 0.5 mol of sulphuric acid, were all purchased from R&M Chemical, and used as received. Deionized water (DI water) and distilled water were obtained using a FAVORIT W4L machine. The Nafion solution, Platinum Carbon (Pt/C 20 wt. %) and Nafion per-fluorinated membrane were all purchased from Sigma Aldrich. Carbon cloth or carbon membrane and Teflon sheets were purchased from Fuel Cell Store. All starting materials were purchased in chemically pure form.

EQUIPMENT

A Planetary Ball Mill Pulverisette 6 machine, Fritsch Ball Mills, was used for ball milling. Ultrasonic (sonicator) from Wisd Laboratory Instrument Ultrasonic was used in sonication. A hot press machine was purchased from AS ONE. Micro pipette was obtained from Eppendoft Research plus, and Autosample syringes were obtained from Agilent CrossLab. For characterization, the RDE was purchased from HZ-5000 Hokuto Denko, and the Fuel Cell Station from Ohkura Diken. RAMAN Sectroscopy was measured on a Confocal REINSHAW, FESEM on a Carl Zeiss Gemini SEM500 and XRD on an X'Pert PRO MPD PW 3040/60 PANalytical.

PREPARATION OF NITROGEN-DOPED GRAPHENE

Nitrogen-doped graphene was prepared here by ball milling using different parameters. One parameter was the mass ratio of the starting materials (graphite and melamine) as shown in Table 1. The ratios 1:3 and 1:10 were chosen based on literature Leon et al. (2011) and Xue et al. (2015). The ratio 1:0 was chosen as a control, while the ratios 1:1 and 1:5 were chosen middle values.

Beside ratio of the raw material, the ball milling conditions were also studied as summarized in Table 1. For practical purposes, effect of short milling time, at 500 rpm speed, was studied here. Xue et al. (2015) used the 500 rpm milling speed for 48 h, which is practically too long. A much shorter milling time (30 min) has been chosen here. The speed of 100 rpm was chosen for comparison with the higher speed (500 rpm) while using same short duration time (30 min).

Firstly, after starting material mixtures were prepared in the desired ratio, each mixture was placed in the Planetary Ball Mill Machine and operated at conditions described in Table 1. Then, the sample was taken out from ball mill using spatula and was placed in vial and dispersed in 20 mL deionized water (DW). The suspension was then ultra-sonicated for 1 h to produce black homogenized suspension. As can be seen in Figure 1, the resulting graphene is highly dispersible in DW after 1 h sonication.

FIGURE 1. Graphene suspensions from samples prepared at different ball milling speeds for 30 min. (1) at speed 100 rpm, and (2) at 500 rpm. Pictures taken for composite samples dispersed in DW after 1 h sonication

After that, the samples were calcined using a box furnace to remove an excess of melamine. The experiment was repeated with different parameters. All samples were labeled as shown in Table 1. The samples were placed on glass slides before being characterized using XRD and RAMAN Spectroscopy. For characterization using FESEM-EDX, the samples were placed on a Si wafer by adhering them on a carbon tape to ensure that the samples have higher background for transmission electron measurement. The samples were then tested using a RDE to study the ORR activity and stability. The best catalyst among various conditions was chosen to fabricate the Membrane Electrode.

TABLE 1. Sample labelling to differentiate all the sample

Sample name	Mass ratio (g) (graphite : melamine)	Condition of ball milling (rpm/min)
Sample 1	1 : 0	100 / 30
Sample 2	1 : 0	500 / 30
A1	1 : 1	100 / 30
A2	1 : 1	500 / 30
B1	1 : 3	100 / 30
B2	1 : 3	500 / 30
C1	1 : 5	100 / 30
C2	1 : 5	500 / 30
D1	1 : 10	100 / 30
D2	1 : 10	500 / 30

CHARACTERIZATION OF NITROGEN-DOPED GRAPHENE

The nitrogen-doped graphene was characterized here using XRD, RAMAN Spectroscopy, FESEM-EDX, and RDE. XRD was used to identify crystallinity phase based on signals and positions (2θ). RAMAN Spectroscopy analysis was used to identify chemical component, defect, and degree of order based on G and D band. RDE was used to evaluate ORR performances and current potentials. FESEM-EDX was used to capture surface images at nanoscale, and to detect the percentage of chemical elements in the samples in order to identify the types of sample.

ROTATING DISK ELECTRODE (RDE) STUDY

A computerized RDE equipment, with three electrodes: References electrode, working electrode, and counter electrode, was used. 0.5 M of sulphuric acid (H_2SO_4) was used as the electrolyte. The characterization modes used in this study were CV and LSV.

7 µL of the nitrogen-doped graphene catalyst suspension (catalyst ink) was dropped on the glassy carbon electrode substrate. After the ink fully dried, the glassy carbon electrode/composite film was connected to the working electrode which was dipped into H_2SO_4 electrolytic solution. All electrodes and cables were connected, and the electrolyte solution was added and purged with oxygen gas for 30 min. Rest mode was chosen before running for CV and LSV. The optimum time for running rest mode was 80 s. The rest mode is to ensure that the sample was stable. The CV was run in the range -0.2 to 8 V at a scan rate 50 mV/s for 10 cycles. The LSV setting was run in the range 1.0 to -0.2 V with a scan rate 10 mV/s. The same steps were repeated for purging with nitrogen gas (99.99%) flow instead of oxygen flow.

MEMBRANE ELECTRODE ASSEMBLY (MEA) STUDY

The main reason of Membrane Electrode Assembly (MEA) fabrication is to test the catalytic performance of nitrogen-doped graphene. MEA fabrication was achieved stepwise as follows. Firstly, Pt/C catalyst ink was prepared by mixing Pt/C (25 mg) with ethanol (500 mg) and Nafion solution (267.5 µL). The mixture was then sonicated for 15 min. Additional 15 min sonication could ensure homogenizing the ink mixture. Similar steps were followed to prepare nitrogen-doped graphene catalyst ink by replacing the Pt/C with the nitrogen-doped graphene that showed optimal RDE results.

Two Carbon Cloth Membrane sheets were cut with dimensions 2.5 × 2.5 cm. The Pt/C catalyst ink (in ethanol) was brushed on the first Carbon Cloth Membrane (anode) placed on hot plate and heated at 80 ºC to ensure catalyst ink drying and to remove ethanol from the membrane. This is because, ethanol evaporates from mixture at temperature above its boiling point 78 ºC. Same steps were repeated for nitrogen-doped graphene on the other carbon cloth membrane (cathode). after that, the carbon cloth and teflon sheets were placed on both sides of membrane and the system was hot pressed at 10 MPa and 130 ºC for 3 min. The arrangement of steel plate, carbon cloth membrane, teflon sheet and Nafion membrane is shown in Figure 2. The prepared MEA was then tested at the fuel cells Station. The current-potential (I-V) plots (LSV) for each catalyst were measured using HZ5000 and HZ5000-ANA software.
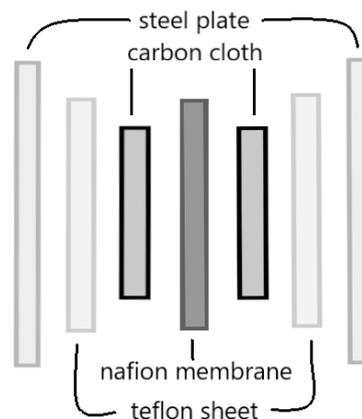

FIGURE 2. The arrangement to fabricate MEA

RESULTS AND DISCUSSION

This section comparatively discusses characterization and performance key results between the lowest ratio and lowest speed of ball milling, sample A1 (1:1, 100 rpm), with the highest ratio and milling highest speed, sample D2 (1:10, 500 rpm).

CHARACTERIZATIONS
COMPOSITE MATERIAL MORPHOLOGY (FESEM)

Figure 3 presents the micrographs of pristine graphite before and after ball-milling process at ratio 1:10 (graphite to melamine mass ratio) with 500 rpm for 30 min. The micrographs show that the ball-milled graphite particles are smaller than non-milled counterparts. The micrographs proved that the ball milling method could reduce graphite to graphene. FESEM instrument was equipped with EDX to detect existing chemical elements in nitrogen-doped graphene.

The morphology for pristine graphite and graphene can be observed using FESEM instrument. The results show that the graphite particle sizes are much larger than those for graphene (Figure 3). This is in congruence with literature (Xue et al. 2015). The element of nitrogen-doped graphene can be identified by EDX analysis. EDX results for different systems are summarized in Table 2.
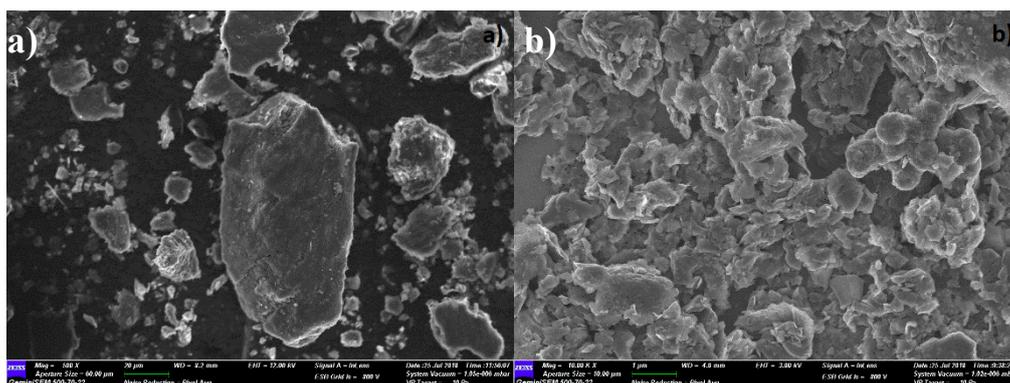
FIGURE 3. FESEM image of raw material graphite a) before and b)
after ball milling

RAMAN SPECTROSCOPY

Table 2 shows the intensity D band/intensity G band (ID/IG) ratios for different prepared composite systems. Nitrogen-doped graphene showed the highest ID/IG ratio while graphite showed the lowest ratio. Figures 4 and 5 show the RAMAN Spectra measured for of both sample A1 (1:1, 100 rpm) and sample D2 (1:10, 500 rpm).

As reported by Xue et al. (2015), graphene and nitrogen-doped graphene Raman spectra showed that the defect (D) band increased for the pristine graphene (G) band compared to graphite. Figure 4 shows the RAMAN spectra measured for samples A1 (1:1, 100 rpm) and D2 (1:10, 500 rpm). As can be seen, the peak of sample A1 (1:1, 100 rpm) represents the graphene peak, based on literature Geng et al. (2011). This indicates that the system essentially involves graphene. The ID/IG ratio for sample A1 (1:1, 100 rpm) is 0.542, which is higher than that for graphite spectra, but still lower than nitrogen-doped graphene as shown in Table 2. Based on FESEM-EDX analysis, nitrogen cannot be observed in sample A1 (1:1, 100 rpm), which confirms the pristine graphene nature of this sample. This is understandable as melamine ratio and milling speed are both relatively low.

Figure 4(b) presents the RAMAN spectrum measured for sample D2 (1:10, 500 rpm). The peak of nitrogen-doped graphene could be observed because the heights of D and G bands were nearly the same. The value of ID/IG of sample D2 (1:10, 500 rpm) 0.991 is higher than for graphite and close to the reported value of nitrogen-doped graphene (1.320). Sample D2 (1:10, 500 rpm) also shows 3.5% nitrogen as confirmed by EDX analysis. The results are encouraging as the 3.5% doping can be achieved within relatively short milling time (30 min only). Compared to earlier nitrogen-doped graphene, with 11.4% (ID/IG =1.320) achieved in too long milling time (Xue et al. 2015) the present results are promising and open way for more investigation to achieve higher doping in short time.

TABLE 2. Different intensity D band/intensity G band (I_D/I_G) ratios for different materials

| Type of catalyst	I_D/I_G ratio	Percentage value for N content in the sample based on FESEM-EDX analysis	Reference
Graphite (raw material)	0.333	0.0	This work
Sample A1 (1:1, 100 rpm)*	0.579	0.0	This work
Graphene*	0.758	0.0	(Geng et al. 2011)
Sample D2 (1:10, 500 rpm)*,	0.991	3.5	This work
Nitrogen-doped graphene**,	1.320	11.4	(Xue et al. 2015)

*30 min milling time, **48 h milling time

The analysis for sample A1 shows that only very little amount of N-doped graphene occurred after ball-milling process. Nitrogen doping did not occur in the resulting graphene sample. This might be due to the minimal period of graphite milling time (30 min) compared to earlier reports (Xue et al. 2015) with 48 h. The low nitrogen doping is due to the presence of added melamine albeit at low ratio. With higher melamine content and higher milling speed, sample D2 (1:10, 500 rpm) showed soundly high nitrogen doping.
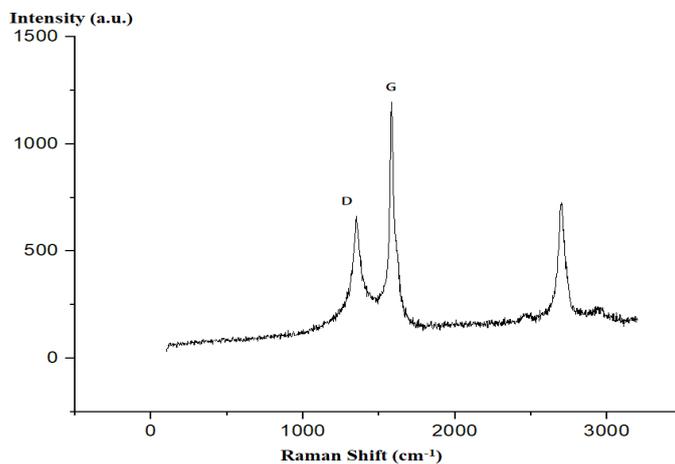
(A)
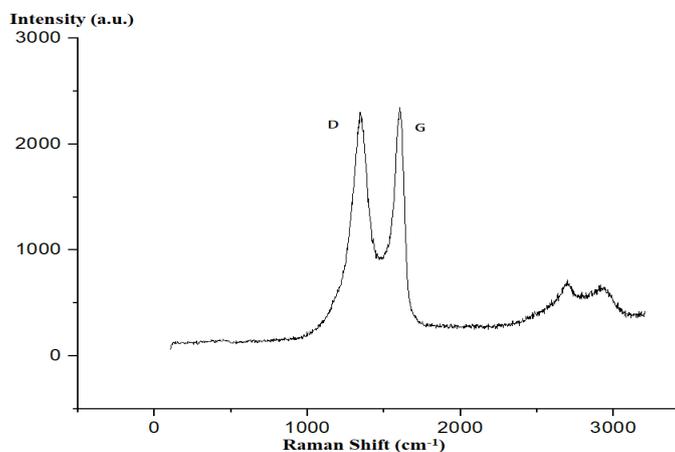
(B)

FIGURE 4. Raman spectra measured for (A) Sample A1 (1:1, 100 rpm) and Sample D2 (1:10, 500 rpm)

X-RAY DIFFRACTION (XRD)

XRD diffraction patterns for different samples are shown in Figure 5. Figure 5(a) describes graphite (raw material) and shows a sharp signal at $2\theta=26°$. This indicates high graphitization degree in the raw material. Figure 5(b) describes melamine (raw material with no graphite) also with a sharp signal. The big broad signals in Figure 5(c), 5(d) and 5(e) are due to glass (glass slide) which is the background signal for the samples during XRD analysis. In Figure 5(d) and 5(e), both sample A1 (1:1, 100 rpm) and sample D2 (1:10, 500 rpm) show a broad signal at $2\theta = 29°$. However, the sample D2 signal (e) is broader than that for

sample A1(d). The XRD patterns confirm the conversion of graphite into graphene, as graphite shows sharper signal than the graphene nano-materials, in congruence with earlier reports (Xue et al. 2015). Nitrogen-doped graphene shows broader signal, than graphene, in the range 2θ=28-30º as described earlier (Geng et al. 2011). Therefore, sample D2 (1:10, 500 rpm) involves nitrogen-doped graphene since the XRD patterns have broader signal compared to sample A1. The difference between the present sample and earlier ones (Xue et al. 2015) was due to difference in ball milling time. This could presumably be due to impurities in the raw materials used. Effect of impurities on nitrogen-doped graphene characteristics needs to be further studied.
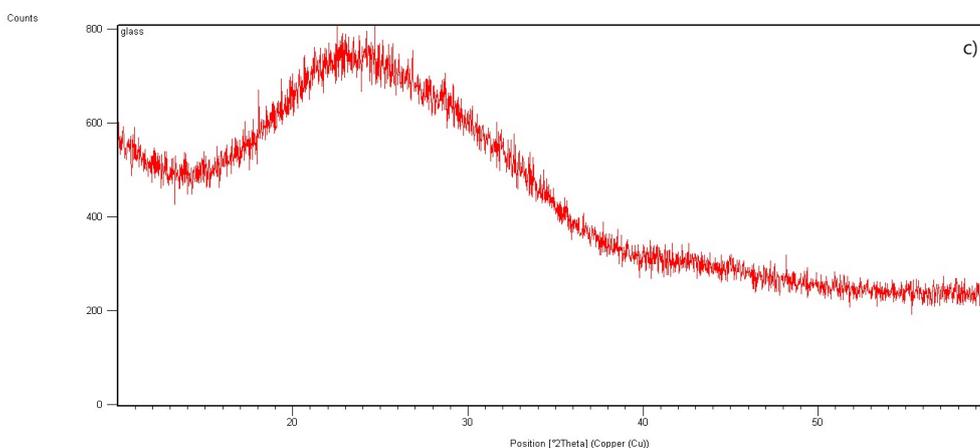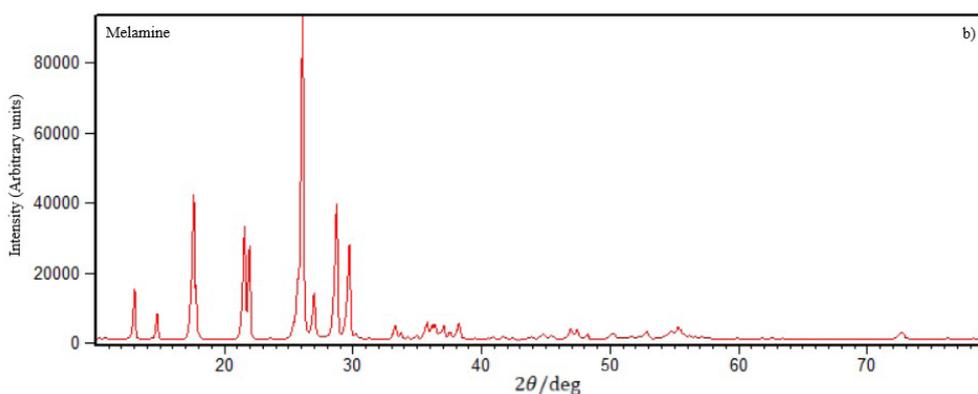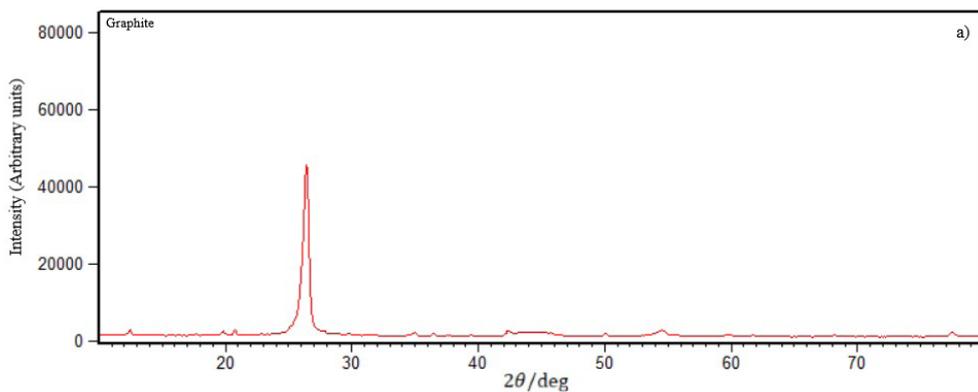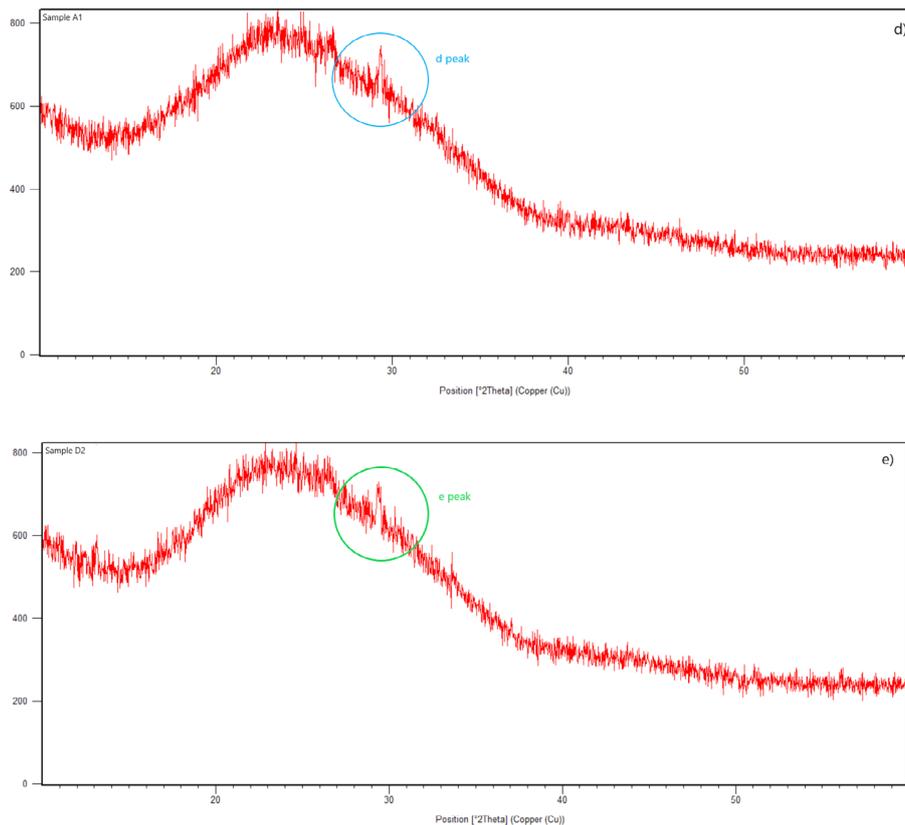
FIGURE 5. XRD patterns of a) pristine graphite, b) raw material of melamine
with no graphite, c) glass slide, d) sample A1 (1:1. 100 rpm), and e) sample D2
(1:10, 500 rpm)

OXIDATION REDUCTION REACTION (ORR) PERFORMANCE RESULTS CYCLIC VOLTAMMETRY (CV)

The ORR performances for A1 and D2 samples were studied using CV. The catalyst was purged with flows of oxygen and nitrogen gases to test CV performance with different speeds of rotating disk electrode. The results show that the speed of the rotation does not affect the CV performance. The type of the prepared sample itself affects ORR performance. Based on Figure 6, sample A1 (1:1, 100 rpm) shows a reduction peak amplitude of 5.5×10^{-5} mA while sample D2 (1:10, 500 rpm) shows a reduction peak amplitude of 8.0×10^{-5} mA. In CV analysis, higher reduction peak amplitude indicates higher performance for ORR (Xue et al. 2015). This means that sample D2 (1:10, 500 rpm) has higher ORR performance than A1 sample. Both ball-milling speed and starting material ratio are the main reasons for the difference between the D2 and A1 systems.
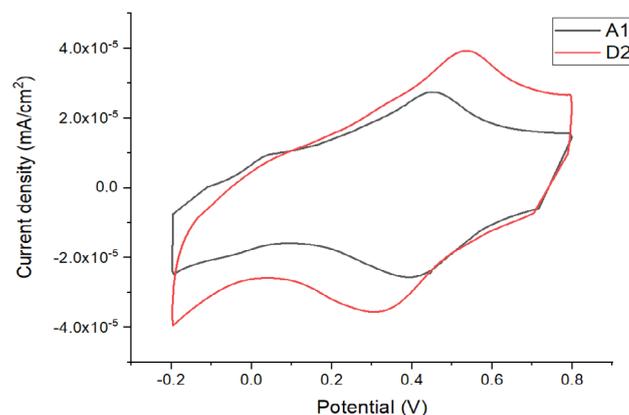

FIGURE 6. CV performance comparison between sample A1
(1:1, 100 rpm) and sample D2 (1:10, 500 rpm)

LINEAR SWEEP VOLTAMMETRY (LSV)

Response to oxygen reduction reaction (ORR) for both A1 and D2 samples has been studied using LSV. The catalyst was purged with oxygen and nitrogen to test the performance of LSV with different speeds of rotating disk electrode. The present results show that the LSV performance varies for different samples independent of the rotation speed. Based on Figure 7, sample A1 (1:1, 100 rpm) showed an ORR performance of 0.125 mA while sample D2 (1:10, 500 rpm) showed higher value of 1.0 mA. Moreover, the graph for sample D2 (1:10,

500 rpm) drops at 1.000 mA while sample A1 (1:1, 100 rpm) drops at 0.125 mA. Sample D2 (1:10, 500 rpm) drop is thus faster than sample A1 (1:1, 100 rpm). The faster the graph drop, the better ORR performance (Xue et al. 2015) which represents the response for Oxygen Reduction Reaction (ORR). Therefore, sample D2 (1:10, 500 rpm) shows good ORR performance because the graph drops faster compared to sample A1 (1:1, 100 rpm). This is mainly due to difference in mass ratio and ball milling speed differences between the two samples.
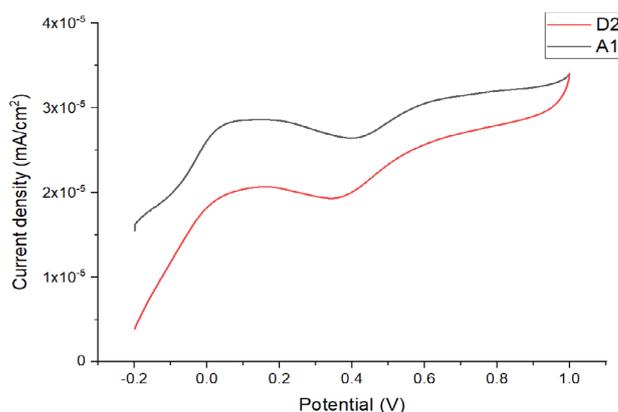

FIGURE 7. Comparison of LSV performance between sample A1 (1:1. 100 rpm)
and sample D2 (1:10, 500 rpm)

MEMBRANE ELECTRODE ASSEMBLY (MEA)

The best catalyst from ORR performance was sample D2 (1:10. 500 rpm) because it showed the highest result compared to other sample. Therefore, catalyst from sample D2 (1:10, 500 rpm) was fabricated on MEA and tested at the Fuel Cell Station. The anode of the membrane was Pt/C and the cathode of the membrane was the nitrogen-doped graphene. The MEA was analysed using HZ5000.

Figure 8 shows that the voltage for sample D2 (1:10, 500 rpm) was 0.14 V compared to 0.813 V for commercial Pt/C. Based on current density vs. potential (J-V) plot, voltage is observed at different currents for sample D2 (1:10, 500 rpm). However, the voltage of commercial Pt/C catalyst was still higher than that for nitrogen-doped graphene catalyst here.
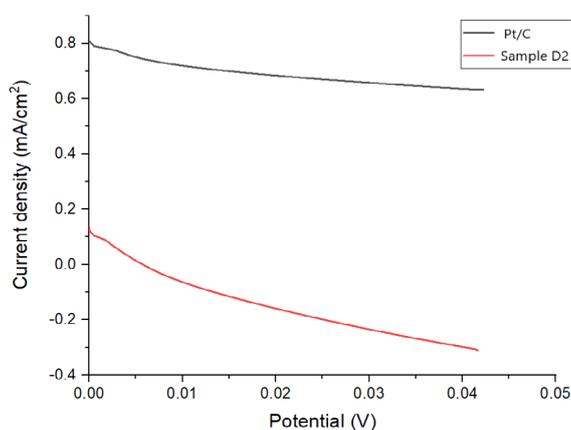

FIGURE 8. Comparison of Pt/C with the best catalyst. Sample D2
(1:10, 500 rpm)

Collectively, the results show the potential of preparing and using nitrogen-doped graphene system which exhibits superior behaviours compared to other pristine graphite and pristine graphene. The nitrogen-doped graphene system characteristics can be further enhanced by increasing melamine content in the starting material and by using longer ball milling time. The nitrogen-doped graphene electrode in MEA fuel cells showed soundly good electrochemical performance, albeit lower than the commercial Pt/C electrode. Further enhancement in the composite electrode can be achieved by further modifications.

CONCLUSION

Nitrogen doped graphene was synthesized by ball milling of graphite with melamine. Based on the ORR result, higher reduction peak for exfoliate nitrogen-doped graphene is observed for the system prepared by higher milling speed (500 rpm) even for short time (30 min) with graphite and melamine ratio at 1:10 (sample D2). The percentage of nitrogen content was 3.5%. The present results showed that higher milling speed and higher melamine amount yield higher nitrogen doping concentration in the synthesized composite. Raman Spectroscopy showed that higher melamine sample prepared with higher milling speed exhibits D and G bands of nitrogen-doped graphene. The XRD pattern showed a broad signal for that sample, which confirmed to the presence of nitrogen-doped graphene. When investigated as MEA electrode, the sample showed open circuit potential V_{OC} value of 0.14 V. The study highlights the value of preparing nitrogen-doped graphene electrodes, for electrochemical applications, simply by ball milling of graphite with melamine. Milling speed and starting material ratio affect the composite characteristics. Therefore, further enhancement in composite characteristics can be achieved by further optimizing preparation parameters.

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