Effect of nitrogen doping on graphite cathode for hydrogen peroxide production and power generation in MFC

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ABSTRACT

Microbial fuel cell is a sustainable and renewable technology which commonly uses graphite as cathode for hydrogen peroxide production. One of the limitations of using graphite cathode is the slow kinetics of oxygen reduction reaction. Nitrogen doping has been demonstrated to be an efficient approach to regulate the electronic as well as surface characteristics of graphite cathode. Therefore, in this study nitrogen doping of graphite cathode was performed to determine the feasibility of H2O2 production and energy generation in a dual chamber MFC. An integrated approach of quantum chemical calculation in combination with experimental investigation was used. Quantum chemical calculations confirmed the production of H2O2 with the lowest Gibbs's free energy of −63 kcal/mol. For validation, ammonia treatment of graphite cathode was performed. The XPS analysis of doped cathode revealed the presence of Graphitic-N functionalization with overall N1s content of 2.96%. Cyclic voltammetric analysis of nitrogen doped cathode further confirmed the production of H2O2 at the peak current value of −4.0 mA and on-set potential of −0.55 V. Following CV analysis, hydrogen peroxide production experiments were performed in a dual chamber MFC. Maximum of 175 mg/L of H2O2 was obtained with simultaneous power generation of 47.61 W/m2, indicating the synergetic effect of nitrogen doped cathode. Thus, from the findings of quantum chemical evaluation and experimental investigation, it is concluded that nitrogen doping of graphite cathode is an efficient approach to improve the performance of MFC in terms of H2O2 production and power generation.

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1. Introduction

Fenton oxidation, a type of advanced oxidation processes (AOPs), is an efficient treatment method for recalcitrant wastewaters. It uses iron salt (Fe^{2+}) and hydrogen peroxide (H2O2) in acidic medium and hydroxyl radical (·OH) is produced which enables complete mineralization of recalcitrant organic compounds [1,2]. Nevertheless, the industrial applications of Fenton oxidation are limited due to high treatment cost, mainly contributed by the cost of H2O2 [3] and excessive sludge formation [4]. Commercially grade H2O2 costs $300–500 per ton [5] and approximately 0.63 kg of H2O2 costing around $0.37, is required to treat 1 ton of wastewater [6]. Apart from the economical aspect, transport and storage of excess amount of H2O2 is dangerous as it is classified as oxidizing substance under “division 5.1” by United Nations [7].

To overcome these economic and safety challenges, several researchers have suggested in-situ production of H2O2/HO· as an alternative option, which can probably be achieved through AOPs [8–10]. Production of H2O2 with simultaneous regeneration of Fe^{2+} is possible in electrochemical fuel cells. Nevertheless, this process utilizes higher energy which limits its application for recalcitrant wastewaters [11]. Therefore, a sustainable and energy efficient system is required. In this regard, microbial fuel cell (MFC) is a sustainable and energy efficient technology, which is emerging as a substitute to AOPs for in-situ H2O2/HO· production [12,13]. MFC uses exoelectrogenic bacteria present in the wastewater to convert chemical energy into electrical energy which can partly be used to perform oxygen reduction reaction (ORR) in the cathode chamber. Here, O2 is reduced by following two different pathways leading to the formation of H2O2 or water (Eqs. (1 and 2)) [14].

Path-1

\[ \text{O}_2 + \text{H}^+ + \text{e}^- = \text{HO}_2^+ \quad (1a) \]
HOO$^-$ + H$^+$ + e$^-$ = H$_2$O$_2$

Path-2

\[ \text{O}_2 + \text{H}^+ + \text{e}^- = \text{HOO}^- \] (2a)

\[ \text{HOO}^+ + \text{H}^+ + \text{e}^- = \text{HO}^+ + \text{HO}^- \] (2b)

\[ 2\text{HO}^+ + 2\text{H}^+ + 2\text{e}^- = 2\text{H}_2\text{O} \] (2c)

The potential of MFC for H$_2$O$_2$ production was first explored by Zhu and his co-worker Ni [12] in 2009. They reported that the use of carbonaceous material to replace expensive platinum cathode could significantly increase the probability of H$_2$O$_2$ production in the cathode chamber. However, due to poor catalytic properties of carbonaceous materials and slow kinetics of ORR, higher yields of H$_2$O$_2$ have not been attained [15]. In order to achieve high kinetics for ORR, nitrogen doping has proven to be an efficient approach [16]. In principal, nitrogen functionalization not only regulates the electronic properties of carbonaceous materials but it also tailors the electro-active surface area of graphite/graphene cathode by forming up-to five valence bonds with adjacent carbon atoms [17,18]. Among nitrogen doped structures, pyrrolic and pyridinic nitrogen were reported to play an important role in improving the kinetics of ORR. Furthermore, graphic nitorgen has been demonstrated to have a comparable performance with Pt/C catalyst [19]. The role of graphitic N was further confirmed by Ni and his coworkers who reported its higher performance for ORR and power generation [20]. While nitrogen functionalization results in power improvement, so far the application of nitrogen doped cathodes for H$_2$O$_2$ production has not been addressed.

Determining the possibility of H$_2$O$_2$ production in MFC using nitrogen doped graphite cathode is experimentally challenging due to slow microbial activity and longer start-up times. Over the past few decades, ab-initio quantum chemistry has become a useful tool for improved understanding of complex systems prior to experimental observation. Quantum chemistry predictions in combination with experiments have emerged as an effective methodology for accelerating the development of systems like MFC [21]. The fundamental concept of this method is the solution of Schrodinger equation. The ability of quantum chemical calculations to find an accurate solution for Schrodinger equation has made it possible to address complex problems in multiple disciplines. Thus, it provides a theoretical framework to predict the chemical properties with an advantage of not requiring a huge database. Instead, structure of a molecule is required as an input to GAUSSIAN software for estimating its chemical properties. As an output, structural properties of molecules such as total energy and electronic properties are obtained. Therefore, quantum chemical calculations have been recognized as the most suitable and widely used method to investigate the molecular configuration, electronic structures, reactivity and interactions of the reactants, intermediates and products participating in a particular reaction. Furthermore, with the help of frequency calculations, thermodynamic properties such as Gibbs free energy (\( \Delta G \)) and heat of reaction (\( \Delta H_r \)) can be obtained which are helpful to determine the thermodynamic feasibility of a chemical reaction. Therefore, quantum chemical calculations will be a helpful tool to understand the oxygen reduction reaction (ORR) mechanism and confirm the feasibility of H$_2$O$_2$ production at the surface of graphite and modified graphite cathode. Literature related to quantum chemical calculations for ORR using nitrogen doped graphite rod has increased [22–25]. In these published work, density functional theory (DFT) was used to study the mechanism of H$_2$O/H$_2$O$_2$ production in fuel cells. All of these works mainly focus on ORR mechanism, surface defects and effect of nitrogen functional group on the performance of ORR. Neither of the studies has demonstrated the feasibility of H$_2$O$_2$/H$_2$O production and computational model validation through characterization and experimentation.

Therefore, the aim of this study is to (i) determine the thermodynamic feasibility of H$_2$O$_2$ production at the surface of nitrogen doped graphite cathode using quantum chemical calculations; (ii) Ammonia treatment of graphite cathode; (iii) Validation of proposed GR-N structure through a binding energy approach by using XPS analysis and (iv) experimental determination of H$_2$O$_2$ production in dual chamber MFC using nitrogen doped graphite as cathode.

2. Quantum chemical calculations

2.1. Computational details

Oxygen reduction reaction (ORR) at cathode surface involves a series of electron and proton transfer processes [14]. The elementary steps involve the reduction of chemisorbed O$_2$, kinetically limiting step, to form an adsorbed OOH intermediate. The possible scenario includes O$_2$ coordination to a carbon atom adjacent to the doped nitrogen followed by C–O and O–O bond scission. C–O bond scission after further protonation results in the formation of OOH-complex (Graphene–OOH). Graphene–OOH complex, after O–O bond cleavage, results in the formation of hydrogen peroxide. However, in another scenario, Graphene–OOH complex undergoes CO–OH bond scission which leads to the formation of Graphene–OH complex and water molecule. In subsequent step, Graphene–OH undergoes bond scission together with protonation and leads to the formation of second water molecule according to reaction Eq. (2c) [19].

By considering the mechanistic details on bond cleavage for ORR, possible geometries of reactants, intermediates and products were assumed. The molecular structures and properties of the chemical species involved in oxygen reduction reaction (ORR) are provided in Appendix as Table A1. Geometry optimization and frequency calculations of the selected molecules were performed and thermodynamic feasibility of H$_2$O$_2$ production was determined before experimentation in MFC.

Quantum chemical calculations presented in this work were performed using GAUSSIAN 09W software package [26] and GaussView 05 visualization program [27] was used to generate initial geometries of the selected molecules. Geometries of the selected molecules were optimized at both HF and B3LYP levels using 6–31G* basis set and the corresponding energies were calculated. Since HF considers electron repulsion as an average over the whole molecular orbital, it was employed to obtain the initial geometries only. Therefore, the geometries obtained corresponding to the lowest energy minima in the potential energy plots were used as structures for optimization and frequency calculations at higher levels of theory.

Since the choice of basis set and method requires a compromise between accuracy and computational time, Becke-style three-parameter Density Functional Theory [28] with the Lee–Yang–Parr correlation function (B3LYP) was chosen for the detailed analysis. This is because, calculations at B3LYP level incorporates electron–electron repulsion between the electrons of same and different spins, respectively. It also shows a good accuracy for the complex systems such as radicals containing transition metal atoms at reduced cost and optimum simulation time [29]. Furthermore, 6–31G* was used as basis set due to its potential to calculate the accurate geometries for a large number of organic compounds [30]. All calculations were performed using water as solvent and Dell computer was used as workstation with a 2.70 GHz dual processor, 16 GB Ram and 64-bit operating system.
2.2. Thermodynamic feasibility of H$_2$O$_2$ production

In Quantum chemical calculations, the vibrational frequencies along with the optimized geometry can be employed to obtain a variety of thermodynamic properties. In GAUSSIAN 09 W Software, the concept of statistical thermodynamics i.e. Boltzmann distribution and Partition function is used to compute thermochemical data. The partition function is like a thermodynamic wave function because it contains all thermodynamic properties of a system, just as quantum mechanical wave function contains all the dynamic information [31]. Therefore, the equations that are used to calculate the thermodynamic properties consider the contribution of rotational, electronic, translational and vibrational motions of the chemical species.

Gaussian provides all thermodynamic parameters of an optimized geometry and it uses simple equations rather than considering the individual contribution of rotational, translational, vibrational and electronic motion. The commonly investigated thermodynamic parameters include dipole moment, enthalpy, entropy, Gibbs free energy and heat capacity value. Therefore, the common way of calculating enthalpy of any chemical reaction is:

$$\Delta H^\circ(298K) = \sum_{\text{prod}} \Delta_H^\circ - \sum_{\text{react}} \Delta_H^\circ$$  (3)

In the same way, Gibbs free energy can be calculated as:

$$\Delta G^\circ(298K) = \sum_{\text{prod}} \Delta G^\circ - \sum_{\text{react}} \Delta G^\circ$$  (4)

The free energy function provides an improved insight into the thermodynamic driving functions that influence the reaction and determines the feasibility of a chemical reaction under a particular condition. Theoretically, a reaction is thermodynamically favorable and spontaneous if $\Delta G$ and $\Delta H$ for a given reaction are negative. On the other hand, a positive $\Delta G$ is characteristic of non-spontaneous reaction while a positive $\Delta H$ characterizes an endothermic reaction that requires energy from the surroundings.

3. Experimental studies

3.1. Chemicals and reagents

All chemicals used in this work were of analytical grade and used without further purification. Anaerobic sludge collected from Palm oil production plant near Pahang, Malaysia, was used as an inoculum to accumulate electrochemical active bacteria in the anode chamber. Other chemicals such as sodium acetate (99%), sodium hydrogen phosphate (99%), monosodium phosphate (99–102%), potassium chloride (99%), ammonium chloride (99%), potassium ferricyanide (99%) and sodium sulfate (99%) were procured from Merck Sdn Bhd, Malaysia while potassium permanganate (99%) was purchased from sigma Aldrich Sdn Bhd, Malaysia.

3.2. Cathode modification and characterization

Pure graphite rod with dimension 6 cm × 2 cm was tested as cathode and cathodic support in MFC. It was initially soaked overnight in pure acetone to eliminate the potential impurities from its surface. Later, it was washed with distilled water for future use and modification. This pre-treated rod was labeled GR-CA.

Ammonia gas treatment of GR-CA was conducted in a hollow tubular reactor fixed in a tubular furnace. The schematic representation of tubular reactor is shown in Fig. 1. As shown in Fig. 1, a sieve plate fixed at the bottom of the reactor was used to support GR-CA for ammonia treatment. For safety and control purposes, temperature and pressure sensing probes were installed at the top of the reactor. The temperature was continuously controlled and monitored through a control panel adjacent to the reactor assembly. Furthermore, a vent valve provided at the top of the reactor was used to facilitate gas ventilation in the case of emergency.

For ammonia treatment, GR-CA was placed within a reactor and furnace temperature was ramped up to 700 °C at 50 °C/min using helium (50 mL/min) as an inert gas [32]. After temperature adjustment, the gas feed was switched to 10% NH$_3$ in helium gas. The sample was held at 700 °C for 2 h, before being cooled back to room temperature using helium gas as a cooling medium. The ammonia treated graphite rod was washed three times with distilled water before being used in MFC for H$_2$O$_2$ production. The ammonia treated graphite rod was labeled GR-NH$_3$.

The surface morphology of GR-CA and GR-NH$_3$ was studied using scanning electron microscope “Phenom ProX SEM”. The surface characteristics of the samples were investigated by X-ray photoelectron spectroscopy (XPS). The binding energies obtained as a result of XPS, were used to validate the graphene-N model employed to perform quantum chemical calculations. X-ray photoelectron spectroscopy (XPS) was studied using an ULVAC-Phi Quantera II with a 32-channel Spherical Capacitor Energy Analyzer (SCA) under vacuum (1 × 10$^{-6}$ Pa) using a monochromatic Al Ka (1486.86 eV) and natural energy width of 680 meV. The carbonaceous C 1 s line (284.6 eV) was used as a reference to calibrate the binding energies.

3.3. MFC configuration

A dual chamber MFC was constructed using two Pyrex glass bottles, each with a total volume of 250 mL. Anode and cathode electrodes made of graphite material were soaked overnight in acetone to eliminate the potential contaminants from its surface. Anode chamber was filled with the heat treated graphite granules (at 450 °C for 30 min) [33] and a heat treated (at 450 °C for 120 min) graphite rod (6 cm × 1 cm) was used for external contact and electron collection. During start-up time, heat treated (at 450 °C for 120 min) graphite rod with dimensions same as that of anode was fixed to serve as cathode. Later, it was replaced with GR-NH$_3$ to study the effect of cathode modification on H$_2$O$_2$ production. The distance between anode and cathode was fixed at 9 cm. Anode and cathode chambers were separated by using a pretreated proton exchange membrane [34], Nafion 117, with cross sectional area of 8.5 cm$^2$. The Nafion 117 was treated in three different stages each lasted for 1 h. First, it was boiled in distilled water, then in 3% H$_2$O$_2$ solution and finally in 0.5 M H$_2$SO$_4$ solution. Later, it was stored in distilled water before use [34].

3.4. Start-up and operation

The anode chamber of a dual chamber MFC was inoculated with anaerobic sludge collected from the Palm Oil production plant (Pahang, Malaysia). The characterization of anaerobic sludge used in this study is provided in Table 1. Before inoculation, anaerobic sludge was mixed with growth media consisting of 2.5 g/L sodium acetate, 50 mM phosphate buffer solution (4.3 g/L

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value (g/L)</th>
</tr>
</thead>
<tbody>
<tr>
<td>COD</td>
<td>77–82</td>
</tr>
<tr>
<td>Soluble COD</td>
<td>37.5–40</td>
</tr>
<tr>
<td>BOD</td>
<td>20–23.4</td>
</tr>
<tr>
<td>TSS</td>
<td>26.25–28.92</td>
</tr>
<tr>
<td>pH</td>
<td>4.25–4.48</td>
</tr>
<tr>
<td>N</td>
<td>0.4–0.49</td>
</tr>
<tr>
<td>Volatile fatty acids</td>
<td>8.5–10</td>
</tr>
<tr>
<td>Total volatile solids</td>
<td>32.5–38.7</td>
</tr>
<tr>
<td>Oil and greases</td>
<td>3.167–5.193</td>
</tr>
</tbody>
</table>

Table 1 Characterization of POME anaerobic sludge.
Na$_2$HPO$_4$, 2.25 g/L NaH$_2$PO$_4$, 0.13 g/L KCl, 0.31 g/L NH$_4$Cl) and yeast. The volume ratio between the anaerobic sludge and nutrient mixture was fixed at 1:9. The resulting mixture was stirred continuously using magnetic bar and purged with nitrogen to remove any dissolved oxygen. The cathode chamber was filled with potassium ferricyanide (K$_3$Fe(CN)$_6$) solution, which was used as an electron acceptor and pH was maintained at 7 using 50 mM PBS solution. In start-up phase, a fixed resistor of 1000 Ω was used to complete the external circuit of MFC. All the operations were conducted in a batch mode and voltage across the external resistor was recorded each hour using a multimeter (Model MM570A, Extech). After a few successive cycles of inoculation, stable and reproducible voltages were obtained, it means that the MFC has successfully started and is ready to use for H$_2$O$_2$ production experiments.

After a successful start-up, K$_3$Fe(CN)$_6$ solution was replaced with 0.1 M Na$_2$SO$_4$ solution and was continuously sparged with O$_2$ to keep the catholyte saturated with oxygen. In order to study the effect of cathode modification, heat treated graphite rod was replaced with GR-NH$_3$ and H$_2$O$_2$ production tests were conducted. Like anolyte, catholyte was well stirred and sampled each hour to measure the concentration of H$_2$O$_2$. Anode chamber was kept fully covered using aluminum foil to protect the bacteria from visible light. All experiments were performed in a feed-batch mode at room temperature and atmospheric pressure. Since, voltage across the external resistance is in direct relationship with the microbial activity in anode chamber, it was used as a reference to determine the activity of microbes and the time for replacing the anolyte with fresh synthetic feed.

3.5. Analysis

3.5.1. Electrochemical tests

Voltammetric experiments were performed using a conventional three-electrode arrangement to evaluate the reduction behavior of O$_2$ on GR-NH$_3$ cathode. A GR-NH$_3$ cathode with a cross-sectional area of 0.785 cm$^2$ was used as a working electrode (WE) while platinum wire and Ag/AgCl were used as the counter electrode (CE) and reference electrode (RE) respectively. The cyclic voltammetric (CV) measurement of oxygen reduction on GR-NH$_3$ cathode was performed in 0.1 M Na$_2$SO$_4$ deoxygenated and oxygenated solutions, prepared by sparging pure N$_2$ and O$_2$ respectively. Here, deoxygenated Na$_2$SO$_4$ solution was used as blank to record the background curve. In this study, CV measurements were conducted in the range of 0.4 V to −0.8 V at a scan rate of 0.05 mV/s (30 °C) and reaction time of 2 h.

In addition, a potential step test was performed to understand the electrochemical behavior of oxygen reduction reaction (ORR) at the surface of GR-NH$_3$ electrode. The resulting data was used to calculate the number of electrons transfer in oxygen reduction reaction. Thus, Cottrell equation was used and number of electrons transfer were obtained from the slope of the Q versus t$^{1/2}$ plot.

$$Q = 2nFACD^{1/2}π^{-1/2}t^{1/2}$$

where, Q is coulombs (C), n is no of electrons per mole of oxygen reduced, F is Faraday’s constant (96,485 C/mol), C is the concentration of dissolved oxygen, D is the oxygen diffusion co-efficient, A is the area of the cathode (0.785 cm$^2$) and t is the reaction time (s).

The current efficiency (CE) of H$_2$O$_2$ production, also called as Faradic efficiency can be calculated from following Eq. (6) [35]:

$$CE(\%) = \frac{nFCV}{Q} \times 100$$

where, n is the no of electrons per mole of oxygen reduced, F is Faraday’s constant (96,485 C/mol), C is the concentration of H$_2$O$_2$ in catholyte, V is the volume of electrolyte (0.2 L) and Q is charge in coulombs. Tafel plot was plotted to calculate the exchange current density, an important kinetic parameter used to represent electrochemical reaction rate at equilibrium. Following equation
was used to describe the relationship between the activation potential ($\Delta V_{act}$) of ORR and current density [36]:

$$\Delta V_{act} = a + b \log i$$  \hspace{1cm} (7)

where $a = -2.3 \left( \frac{RT}{F n} \right) \log i$ and $b = 2.3 \left( \frac{RT}{F n} \right)$

Here, $\log i$ is the log-units of the exchange current density (mA/m$^2$), $R$ is the ideal gas constant (8.31 J/mol K), $F$ is the Faraday’s constant and $\alpha$ is the electron transfer co-efficient of ORR.

The voltage ($V$) across the fixed external resistance ($R_{ext}$) was recorded using multimeter (Extech, USA). The current across the external resistor was calculated from $I = V/R_{ext}$ and the calculated values were normalized to the effective volume of the cathode chamber to obtain the current density ($I$). Subsequently, power density ($P$) was calculated using $P = V^2/R_{ext}$.

3.5.2. Chemical analysis

A digital pH meter (Cyberscan pH 300, Eutectic instruments) was used to measure the anodic and cathodic pH of MFC. The cathodic H$_2$O$_2$ concentrations were determined titrimetrically using KMnO$_4$ as a titrant. Simultaneously, COD measurement of the anolyte was also conducted to observe the relationship between H$_2$O$_2$ production and COD reduction when $R_{ext}$ was adjusted at 50 $\Omega$.

COD measurement of the raw and treated samples was made using dichromate closed flux according to the standard method [37]. For this purpose, the required amount of sample filled into the COD test cells (supplied by Merck) was heated in a thermostatic bath for 2 h. After digestion, the COD test cells were removed and cooled down to room temperature. Subsequently, these test cells were analyzed in a UV-spectrophotometer for COD measurement. The COD removal efficiency of the digested samples was calculated as follows:

$$\text{COD(%) = } \left( 1 - \frac{\text{COD}}{\text{COD}_0} \right) \times 100$$  \hspace{1cm} (8)

where COD$_f$ and COD$_0$ represent the final and initial COD values of the samples.

4. Theoretical results and discussion

4.1. Geometry optimization

For performing quantum chemical calculations, identification of the accurate molecular structure is a pre-requisite. Since, graphite has a layered, honey comb like planer structure, geometry optimization of such an infinite structure is not possible. Therefore, a single-layered graphene sheet containing fourteen hexagonal rings with delocalized $\pi$ electrons and terminated C-H bonds was considered. For modeling nitrate graphene-sheet (nitrogen doped graphene sheet), a nitrogen atom substituted in the middle of graphene sheet was considered [25,38]

Based on the developed methodology, geometry optimization and re-optimization of the molecules participating in ORR were performed at ground state using HF/6-31G* and DFT/6-31G* levels respectively. For the purpose, reaction scheme presented as Eqs. (1) and (2) were considered. Since, H$^+$ ion is unstable in nature and can only be optimized in gaseous phase, H$_2$O$^+$ ion a stabilized form of H$^+$ ion in aqueous medium, was considered for geometry optimization and frequency calculations. The fully geometry-optimized structures of the selected molecules are presented in Fig. 2. Besides, total electronic energies and geometric parameters of the reactants, intermediates and the products formed as a result of ORR are provided in Table 2. Since, the resulting geometries obtained the lowest energy minima during the optimization process, the geometries are stable and can thus be used to perform the further analysis such as binding energy calculations and thermodynamic analysis of ORR.

<table>
<thead>
<tr>
<th>Quantum parameters</th>
<th>Total energy (kcal/mol)</th>
<th>HOMO energy (eV)</th>
<th>LUMO energy (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphene</td>
<td>-1,020,90,413</td>
<td>-3.93</td>
<td>-1.54</td>
</tr>
<tr>
<td>Oxygen</td>
<td>-94,249,53</td>
<td>-6.59</td>
<td>-4.65</td>
</tr>
<tr>
<td>H$_2$O$^+$</td>
<td>-1,115,165,60</td>
<td>-4.39</td>
<td>-1.98</td>
</tr>
<tr>
<td>HOO$^-$</td>
<td>-48,196,84</td>
<td>-13.19</td>
<td>-0.49</td>
</tr>
<tr>
<td>HO$^*$</td>
<td>-1,115,595,20</td>
<td>-4.62</td>
<td>-2.16</td>
</tr>
<tr>
<td>Water</td>
<td>-1,068,470,08</td>
<td>-4.54</td>
<td>-2.01</td>
</tr>
<tr>
<td>H$_2$O$_2$</td>
<td>-95,080,36</td>
<td>-6.01</td>
<td>2.09</td>
</tr>
</tbody>
</table>

Table 2: Quantum chemical parameters calculated at B3LYP/6-31G* level.

<table>
<thead>
<tr>
<th>Reactions</th>
<th>$\Delta H$ (kcal/mol)</th>
<th>$\Delta G$ (kcal/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Path-1 (H$_2$O$_2$ formation)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>O$_2$</td>
<td>-33.24</td>
<td>-21.84</td>
</tr>
<tr>
<td>R-2a</td>
<td>-98.8</td>
<td>-83.57</td>
</tr>
<tr>
<td>R-2b</td>
<td>-66.39</td>
<td>-63.06</td>
</tr>
<tr>
<td>Path-2 (H$_2$O formation)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>R-3a</td>
<td>-98.8</td>
<td>-82.57</td>
</tr>
<tr>
<td>R-3b</td>
<td>-56.85</td>
<td>-51.35</td>
</tr>
<tr>
<td>R-3c</td>
<td>-114.46</td>
<td>-106.70</td>
</tr>
</tbody>
</table>

Table 3: Gibbs free energy and heat of reaction for H$_2$O$_2$/H$_2$O production.

4.2. Thermodynamic feasibility of H$_2$O$_2$ production

For thermodynamic feasibility analysis, frequency calculations of the optimized geometries were performed. As a result, thermodynamic properties such as Gibbs free energy and heat of formation were obtained, which were used to define the most favorable path for a specific chemical reaction. Based on the reaction scheme presented as Eqs. (1) and (2) and information available in literature, water and H$_2$O$_2$ are possible products formed as a result of ORR [13,39]. As per the reaction Eqs. (1(a and b) and 2(a–c), heat of reaction and Gibbs free energies were calculated for Graphene-N cathode. Calculated values are shown in Table 3 and a concise comparison of $\Delta H$ and $\Delta G$ is represented as Fig. 3. From the data provided in Table 3, it was observed that all the values for heat of reaction and Gibbs’s free energy changes are negative which confirm that both the production of H$_2$O$_2$ and water is thermodynamically favorable and spontaneous at the surface of Graphene-N cathode.

A comparison of Gibbs’s free energy represented in Fig. 3 showed that R-2c i.e. water formation reaction step in the reaction pathway 2 is the most favorable with the $\Delta G$ of $-106.70$ kcal/mol and R-2b with the $\Delta G$ of $-51.35$ kcal/mol is the least favorable and less spontaneous. However, a step-wise analysis of free-energies shows that the probability of H$_2$O$_2$ formation is higher than water in the presence of Graphene-N. The first step which involves the production of HOO$^-$ complex is the same for both types of reaction with the $\Delta G$ of $-63.06$ kcal/mol. On the other hand, H$_2$O$_2$ production followed by second electron oxygen reduction had lower $\Delta G$ value i.e. $-63.06$ kcal/mol compared to the water formation in the second step of Path 2. As smaller $\Delta G$ value is desirable for rapid and spontaneous reactions, H$_2$O$_2$ should be thermodynamically feasible.

From the thermodynamic analysis, it is concluded that H$_2$O$_2$ production is the most feasible reaction and would follow the lower energy pathway in the presence of Graphene-N cathode. Therefore, nitrogen doped cathode would be the suitable cathode in MFC for H$_2$O$_2$ production. In summary, it is concluded that quantum chemical calculations are useful tool to provide a clear understanding of a reactive system before experimentation. It is
ahead of experimental design since it can predict the feasibility of chemical reaction without experiments and huge data base.

5. Experimental results and analysis

5.1. Surface characteristics of ammonia treated graphite cathode

The scanning electron micrographs (SEM) for graphite (GR-CA), and ammonia treated graphite (GR-NH₃) cathodes were taken using “Phenom ProX SEM” as shown in Fig. 4. The SEM images illustrate a distinct difference in the morphology of cathode materials. In comparison, GR-NH₃ rod had fibrous like structure with well-defined cracks on its surface. The formation of cracks is more likely due to the heat treatment of GR-NH₃ rod at 700 °C [40]. Studies showed that crack formation results in an increase in the surface area which could enhance the power density as well as H₂O₂ production if the materials had same characteristics [33]. However, it is still unknown that to what extent changes in surface chemistry caused by ammonia treatment, will affect both H₂O₂ production and power generation.

Nitrogen doping has been demonstrated to be an effective approach to improve the catalytic properties of graphite cathode for ORR [25]. Introduction of nitrogen functional groups not only regulate the electronic properties of graphite cathode but also increase the probability of two-electron ORR [19,41]. In order to confirm the presence of nitrogen functional groups, XPS analysis of GR-CA and GR-NH₃ cathodes was performed. The XPS analysis in Table 4 confirmed the presence of C, N and O on the surface of GR-NH₃ cathodes. However, only C was observed on the surface of GR-CA material. Based on XPS analysis, atomic ratios N1s/C1s and O1s/C1s

![Fig. 2.](image-url)
ratio were calculated which were found to be 0.035% and 0.141% respectively. In comparison with the previous studies, an increase in N1s/C1s and O1s/C1s ratios was observed, implying that ammonia treatment is an effective approach to modify the properties of graphite cathode [33,40]. Beside chemical composition, XPS results were further analyzed to confirm the chemical state of nitrogen functional groups. The full XPS spectrum of GR-CA and GR-NH3 cathode is shown in Fig. 5.

Comparison of XPS spectrum for GR-CA and GR-NH3 showed that O1s showed two peaks at 531.23 and 533.45 eV, reflecting the presence of C=O and C–O respectively (Fig. 6(a)). However, in the case of GR-NH3, the peak at 533.45 eV was weakened, indication
the reduction of C–O to C=O during ammonia treatment. The N1s spectra showed in Fig. 6(b) marked maximum peak at BE ≈ 400 eV. This signal is assigned to presence of quarternary-N species by which each N atom is bonded with three carbon atoms within graphite plane, hence, they are also known as ‘graphitic nitrogen’ species [42–44]. In previous works, graphitic nitrogen has been demonstrated to have a comparable performance with Pt/C catalyst [19].

Following chemical composition analysis, XPS results were used to validate the accuracy of GR-N geometry used to perform quantum chemical calculations. For this purpose, binding energy approach was used. For binding energy calculations, the electronic energies obtained by optimizing GR-N and GR were used to calculate binding energies as follows:

$$\Delta E_{\text{binding}} = \sum_{\text{product}} E - \sum_{\text{Reactants}} E$$

where,

$$\sum E = \text{sum of the electronic energies of the products (i.e. graphene-N and C)}$$

$$\sum E = \text{sum of the electronic energies of the reactants (i.e. graphene and N)}$$

For binding energy calculations, GR-N and C were considered as products while GR and N were considered as reactants. The calculations were performed and 454.656 eV binding energy was obtained. The value obtained as a result of theoretical calculations was close to the experimentally obtained value i.e. 400 eV, implying the accuracy of proposed molecular geometry with the experimental results.

In summary, the findings of elemental analysis confirm that ammonia treatment of GR-NH$_3$ cathode is an effective approach to change the surface chemistry. However, it is still unknown that to what extent changes in surface chemistry caused by ammonia treatment, will affect both H$_2$O$_2$ production and power generation. To support this argument, in this work, electrochemical studies were conducted to further confirm and validate the findings of surface characterization as well as quantum chemical calculations.

5.2. Electrochemical studies

Cyclic voltammetry scans were performed to examine the reduction of O$_2$ at GR-NH$_3$ cathodes using 0.1 mol/L Na$_2$SO$_4$ oxygenated and deoxygenated solutions. The voltage was scanned...
Counts

C-O (GR)

C-O (GR-NH)

C-O (GR-NH) 3

(b)

Counts

N 1s

binding Energy (eV)

395 400 405

Fig. 6. X-ray photoelectron spectra collected for GR-CA and GR-NH3 cathode sample (a) O1s (b) N1s.

between −0.8 V and 0.4 V at a predefined scan rate of 0.01 V/s. The cyclic voltammogram obtained is shown in Fig. 7.

Examination of the cyclic voltammograms reveals that no redox peak was observed when the measurement was performed in deoxygenated Na2SO4 solution (Fig. 7 (curves a)). However, in the case of oxygenated Na2SO4 solution, two obvious reduction peaks were observed with an on-set potential of −0.1 V. It means that if the cathode potential of MFC is lower than −0.1 V, the ORR could take place at the surface of GR-NH3 rods. The shift of on-set potential from a more negative (with graphite rod i.e. −0.15 V [15] to less negative value shows that GR-NH3 rods would perform better than GR-CA.

For theoretical validation and confirmation of final reduction product on GR-NH3 cathode, a detailed examination of reduction peaks was performed. In Fig. 7 (curves b), the potential was observed to be scanned from a positive to negative potential, suggesting the reduction of O2 at the surface GR-NH3 cathode. After approaching the on-set potential value of −0.1 V, reduction of O2 started and the reduction current began to flow. As the potential got more negative, the reduction current started to increase until it reached the peak values of −4.0 mA for GR-NH3 cathode. After the peak current value, it started to decrease and obtained second peak current values at −2.25 mA. Corresponding to first reduction peaks, the potential value of −0.55 V was obtained, suggesting the occurrence of two-electron oxygen reduction to H2O2 [13]. Following the first sharp peaks (−0.55 V, −4.0 mA), oxygen reduction rate was determined by the mass transfer rate of O2 to the electrode surface. The possible accumulation of H2O2 near the electrode surface results in the shift of potential from less negative value of −0.55 V to a more negative value of −0.7 V. As a result, a decrease in the reduction current was observed from −4.0 mA to −2.25 mA. Another reason for a decrease in cathodic current might be the reduction of H2O2 by further two-electron oxygen reduction that generates water [45]. In this study, the first peak current values for both GR-H and GR-NH3 cathode were higher in magnitude as compared to GR-CA. For GR-CA, Fu et al. [15] obtained −0.19 mA peak current while Chen et al. [13] obtained −0.38 mA as peak current using three-dimensional graphite electrodes. According to the fundamentals of CV, higher the peak current, higher will be concentration of the reduced product [46]. Therefore, it can be concluded that graphite cathodes after treatment would produce high concentrations of H2O2 as compared to previous studies conducted by using GR-CA and GR-H cathode [36].

In addition to peak current analysis, potential-step test analysis was performed using GR-NH3 cathode immersed in 0.1 mol/L Na2SO4 oxygenated solution. The O2 concentration was 1.9 × 10−6 mol/cm3. The electrode potential was set between −0.55 V and −0.2 V and number of electron used for oxygen reduction reaction (ORR) was obtained from the slope of the Q versus t1/2 plot. Integrating the data obtained from Fig. 8 and Eq. (5), the slope of the curve for Q (μC) and t1/2 of 4815.5 t1/2 determined n to be 2.27. Note that oxygen following two-electron reduction produces hydrogen peroxide while water is formed as a result of four electron reaction mechanism. Here, the ‘n’ value of 2.27 determines that ORR preferentially follows two-electron step at the surface of GR-NH3 cathode, confirming the selectivity of GR-NH3 cathode for two-electron ORR.

Based on the results obtained, Faraday’s efficiency for H2O2 production was obtained using Eq. (6). Using H2O2 concentration of 5.11 × 10−6 mol/cm3, Faraday’s efficiency was calculated to be 34%. The reason behind lower Faraday’s efficiency may be the result of high internal resistance, biomass accumulation on PEM, energy loses, and large volume of electrolytes.

To further evaluate the performance of MFC for H2O2 production, Tafel plot was used to calculate the exchange current density. It is in turn used to determine how fast the electrochemical reaction occurs at the electrode surface. A graph between the
activation over potential ($\Delta V_{\text{act}}$) of ORR and current density was plotted as Fig. 9. The value of ‘$\alpha n$’ and exchange current density can be calculated from the slope and intercept of the polarization curve (Fig. 9). Thus by integrating the data obtained from polarization curve and equation, the slope of the curve $-787.84 \log i$ determines $\alpha n = 0.074$ and $i = 8.15$ mA/m$^2$. The lower values for ‘$\alpha n$’ determine increase in the value of over potential with increasing current density. Thus, greater potential is required to overcome the activation energy barriers of ORR. In comparison with the study performed by Fu et al. [15], higher values for exchange current densities were obtained. It means that high current densities will be required to overcome the energy loses of the system. Therefore, in this study, the external resistance value was reduced to 50 $\Omega$, which is one of the pre-requisites of $\text{H}_2\text{O}_2$ production in MFC.

5.3. $\text{H}_2\text{O}_2$ production test

Prior to $\text{H}_2\text{O}_2$ production tests, the anode chamber of MFC was inoculated with exoelectrogenic bacteria present in POME anaerobic sludge. During the start-up time, external resistance was maintained at 1000 $\Omega$ and the cathode chamber was filled with $\text{K}_3\text{Fe(CN)}_6$ solution. After 10 h of inoculation, the voltage across the external resistor started to develop. The voltage attained its maximum value of 0.4 V within 4 days of inoculation and was kept stable for 3 successive days. After 1 week, the voltage started to decrease and reached a minimum value of 0.1 V. At this time, MFC was inoculated with nutrient mixture (synthetic feed) and the same procedure was repeated. After three successive inoculations, repeated values for voltage were obtained. It implied that MFC has successfully started and is ready to use for in-situ $\text{H}_2\text{O}_2$ production experiments.

For performing $\text{H}_2\text{O}_2$ produciton experiments, catholyte containing 50 mmol/L of $\text{K}_3\text{Fe(CN)}_6$ solution was replaced with 0.1 M $\text{Na}_2\text{SO}_4$ solution and pH was maintained at 7 using 50 mmol/L of PBS. Heat treated graphite cathode was replaced with GR-NH$_3$ and catholyte was sparged with $\text{O}_2$. The voltage was allowed to get a stable value. After stabilization, catholyte was replaced with fresh $\text{Na}_2\text{SO}_4$ sample and continuously sparged with oxygen. After 12 h, the sample was taken and analyzed for $\text{H}_2\text{O}_2$ concentration. The $\text{H}_2\text{O}_2$ concentration of 152 mg/L was obtained with simultaneous power production of 38.44 mW/m$^2$. In order to investigate the potential of MFC for $\text{H}_2\text{O}_2$ production, $\text{O}_2$ sparging was continued and samples were analyzed each hour for $\text{H}_2\text{O}_2$ concentration. No obvious change in the concentration of in-situ produced $\text{H}_2\text{O}_2$ was observed even the process was prolonged till 22 h. The findings of this experimental test are in consistent with our recently published work (reference) and also with that of CV studies. This is because, longer test duration would likely result in the self-decomposition of $\text{H}_2\text{O}_2$ or its further reduction to water on the surface of graphite cathode [47]. On the other hand, accumulation of $\text{H}_2\text{O}_2$ around cathode surface may limit the diffusion of oxygen to GR-NH$_3$ graphite cathode [13]. Therefore, the experimental time was fixed at 12 h and MFC was allowed to continue its operation for 16 days in a batch mode. The experimental data obtained as a result of 16 days of continuous operation is presented in Table 5. Furthermore, the graphical representation of $\text{H}_2\text{O}_2$ production corresponding to $\Delta \text{COD}_{\text{anode}}$ is also presented as Fig. 10.

From the data provided in Table 5 and Fig. 10, a linear trend was observed among $\text{H}_2\text{O}_2$ concentration, power production and reduction in anodic COD concentration. The experimental tests for $\text{H}_2\text{O}_2$ production showed the highest concentration of 175 mg/L. $\text{H}_2\text{O}_2$. The corresponding anodic consumption was 5269 mg/L with simultaneous power production of 47.61 W/m$^2$. On the other hand, 60 mg/L of $\text{H}_2\text{O}_2$ was the minimum concentration that was obtained with the lowest power production of 15.21 W/m$^2$. In comparison with the studies conducted by Modin and Fukushima [47] and Chen et al. [13], higher values for $\text{H}_2\text{O}_2$ concentration and power output were attained in the presence of GR-NH$_3$ cathode. For example, Modin and Fukushima, [47] obtained 9.67 g/L of $\text{H}_2\text{O}_2$ at an energy requirement of 3 kW/kg of $\text{H}_2\text{O}_2$ while Chen et al., [13] achieved 196 mg/L of $\text{H}_2\text{O}_2$. They obtained 196 mg/L of $\text{H}_2\text{O}_2$ after 24 h of continuous operation using an external resistance of 20 $\Omega$. In this work, higher concentrations of $\text{H}_2\text{O}_2$ were obtained because the cracks produced as a result of heat treatment results in an increase in the surface area of the cathode. On the other hand, nitrogen functionalization intrinsically regulates the electronic proprieties of graphite cathode by forming three valence bonds with adjacent carbon atoms [44]. As a result, more electronegative nitrogen removes electron from the adjacent carbon, which acts as the active sites for oxygen reduction reaction [18]. The findings of experiments are also in consistent with that of quantum chemical calculations that nitrogen doping reduces the adsorption energy of the graphite for $\text{O}_2$ which eventually increases the reduction rate of $\text{O}_2$ to $\text{H}_2\text{O}_2$. The adsorption energy values of 65.08 kcal/mol and 23.50 kcal/mol were obtained for the adsorption of oxygen on graphene and graphene-N respectively. Furthermore, lower Gibb’s free energy values (–83.57 kcal/mole) in the rate determining step is also an evidence of $\text{H}_2\text{O}_2$ production at the surface of GR-NH$_3$ cathode.

In summary, the findings of quantum chemical calculations, SEM/EDX, XPS, electrochemical studies and $\text{H}_2\text{O}_2$ production tests confirm that ammonia treatment of graphite rod favors the production of $\text{H}_2\text{O}_2$ in MFC.
6. Conclusion

Nitrogen doping of graphite cathode has been demonstrated to be an effective approach for improving the reaction kinetics of ORR. However, application of nitrogen doped graphite cathode for H$_2$O$_2$ production is still unknown. Therefore, in this study an integrated approach of using quantum chemical calculations and experimental investigation was used to predict and validate hydrogen peroxide production. Theoretical findings reveal that H$_2$O$_2$ with the Gibb’s free energy value of −60 kcal/mol is the most feasible product at the surface of nitrogen doped graphite cathode. The potential of nitrogen doped graphite cathode for H$_2$O$_2$ production was determined using XPS analysis and electrochemical tests. XPS analysis reveals the presence of nitrogem nitrogen with overall N 1s content of 2.98%. Experimentally, 175 mg/L of H$_2$O$_2$ was produced with simultaneous power production of 47.61 W/m$^3$. Therefore, it is concluded that nitrogen doped graphite cathode is proven to be an efficient method in improving the performance of MFC for hydrogen peroxide production simultaneous with power generation.

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