

## DFT Investigation for Better Efficiency of Fuel Cells in Presence of Nitrogen Containing Graphene sheets as Catalysts

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### Abstract

Fuel cells can directly convert chemical energy into electric energy with high conversion efficiency and no pollution. Among many factors affecting the chemical-electrical energy conversion, oxygen reduction reaction (ORR) on cathode is the pivot in fuel cell. This reaction is a kinetically slow process, which dominates the overall performance of a fuel cell. The ORR can proceed through two ways. One is a direct four-electron pathway, in which O<sub>2</sub> is reduced directly to water without involvement of hydrogen peroxide. The other is a less efficient two-step two-electron pathway in which hydrogen peroxide is formed as an intermediate. To achieve a high efficiency fuel cell, the four-electron pathway is expected to occur. Because the ORR process is very slow in nature, catalysts must be used to facilitate the four-electron pathway to boost the efficiency of fuel cells. Traditionally, such electro catalysts are platinum and its alloys, but they are expensive and susceptible to time-dependent drift and CO poisoning, which limits large-scale application of the fuel cell. There have been intensive research efforts to reduce or replace Pt and Pt based alloys electrodes in fuel cell. In this work using calculated NMR and NQR parameters in some nitrogen-containing graphene sheets (with one or two nitrogen), the effect of nitrogen atom on charge density of carbon atoms was studied. The results showed that in the presence of nitrogen, charge density of some carbon atoms decreased and these atoms are better candidate as catalyst active site than pure graphene.

### Keywords

Fuel Cell; Nitrogen-Containing Graphene Sheets; Catalyst; NQR Spectroscopy .

### 1. INTRODUCTION

A fuel cell generates electricity by a chemical reaction at the electrodes. One great appeal of fuel cells is that they generate electricity with very little pollution because the only reaction product is water. However, fuel cells are less durable than petrol and diesel engines, so they are not long-lasting. Moreover, are very expensive. The oxygen reduction reaction (ORR), is one of the fundamental reactions in energy conversion systems such as fuel cells [1-3]. Oxygen reduction in aqueous solutions occurs mainly through two different pathways: either a four-electron reduction pathway form O<sub>2</sub> to H<sub>2</sub>O or a two-electron pathway from O<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>. The four-electron reaction has been recognized as the favored pathway because it has no peroxide species that contribute to certain degradation mechanisms of the electrode and the electrolyte membrane and there are higher operating potentials and current efficiency in the fuel cells [4-7]. Unfortunately, the ORR kinetics is normally very slow. In order to speed up the ORR kinetics to reach a practical usable level in fuel cell, a cathode ORR catalyst is needed. Platinum (Pt)-based materials are the most practical catalysts. But these pt-based catalysts are too expensive for making commercially viable fuel cells and many researches has focused on developing alternative

catalysts, including non-noble metal catalysts [8-10].

Many research efforts has been made to reduce or replace Pt and Pt based alloys electrodes in fuel cell. One of the most important alternative catalysts is carbon nanostructures.

Nuclear Quadrupole Resonance (NQR) spectroscopy analysis [11] is a technique for further understands the bonding nature of atoms. Quadrupolar parameters are very sensitive to electric charge distribution around quadrupolar nuclei ( $I > 1/2$ ). Determination of the charge distribution in molecules or complexes can be done by the quantum mechanical approach as an effective method. In this method, the electric field gradient (EFG) of whole molecular charges can be evaluated at any point in the molecular space. The interaction of EFG and quadrupole moment of quadrupolar nuclei is measured by the nuclear quadrupole coupling constant (NQCC). In this work using calculated NMR and NQR parameters in graphene and some nitrogen-containing graphene sheets (with one and two nitrogen atom), the effect of nitrogen atom on charge density of carbon atoms was studied and by determining of electronic structure of some nitrogen-containing graphene sheets the catalytic effect of these

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compounds in ORR on cathode in fuel cells was studied.

## 2. EXPERIMENTAL

The B3LYP/6-31G computational model as implemented in the Gaussian software package is an effective method for accurate calculation of N-NQCC tensors [12,13]. In this work the results of NMR chemical shifts and NQCC calculations using this model have been reported. The electric field gradient (EFG) at the site of nitrogen atoms were calculated to obtain NQCC parameters using Gaussian 09 [14] at B3LYP/6-31G level of theory. Calculated NQCCs of nuclei are proper way for better understanding of the electronic structure of compounds. NQCC is an appropriate scale for the charge density of atoms. For theoretical calculation of NQCCs, the electric field gradient (EFG) tensor at a nucleus must be calculated. According to NQCC expression, NQCC of nuclei has a direct relation to  $q_{zz}$ .  $q_{zz}$  is the Z component of EFG tensor in principal axes system. Two controlling factors of  $q_{zz}$  are Charge density on the nucleus and symmetry of EFG around the quadrupolar nucleus. The importance of NQCCs is that same nucleus in different molecules have different values of the field gradient. Nitrogen atom with higher charge density has smaller  $q_{zz}$  and consequently less NQCC.

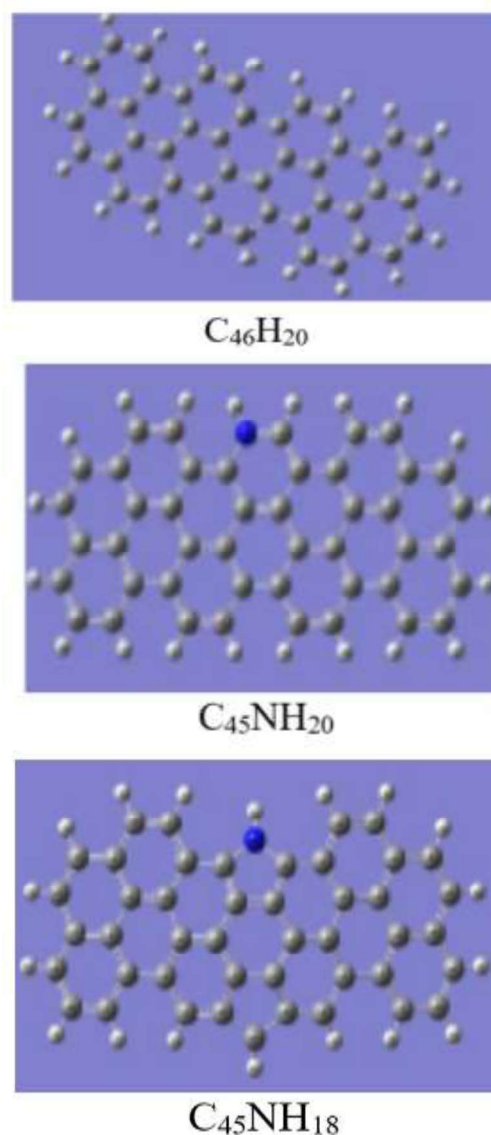
## 3. RESULT AND DISCUSSION

The slow rate of the ORR at the cathode is still a major challenge in the research and development of fuel cells. Pt and Pt based alloys electrodes are the best metal electrocatalysts for the ORR with high activity and durability in acid [15]. Due to the high cost of platinum, attempts are made to suggest more suitable catalysts for ORR process in fuel cells. For example, it is possible to increase the efficiency of fuel cells by creating better conditions for easier four-electron methods in the ORR at the cathode.

In Four-electron ORR mechanism,  $O-O-H^+$  is formed as intermediate [16]. OOH interacts with grapheme (as catalyst) and chemical bond between oxygen and carbon is created. This is the most important step of the catalytic effect of grapheme [17-19]. The formation of bond between OOH and C is necessary to four-electron method and OOH reacts with carbon atoms with less charge density. Therefore, charge density of carbon atoms in

studied graphenes is a criterion for attack of OOH. Carbon atoms with lower charge densities react more easily with OOH. For investigation of the effect of nitrogen atom on charge distribution of carbon atoms of graphene sheets, two different nitrogen-containing graphene sheets ( $C_{45}NH_{20}$  and  $C_{45}NH_{18}$ ) were studied, containing pyridine and pyrrole species, respectively, as shown in Figure 1. For comparison, graphene sheets with the same configuration but no N-doping ( $C_{45}H_{20}$ ) were also constructed.

The calculated NMR chemical shifts and  $^{14}N$ -NQCCs are reported in Table 1.



**Fig. 1.** graphene ( $C_{46}H_{20}$ ) and nitrogen containing graphene sheets ( $C_{45}NH_{20}$  &  $C_{45}NH_{18}$ ) considered in this study

**Table 1.** Calculated chemical shifts and nuclear quadrupole coupling constants of considered graphene sheets.

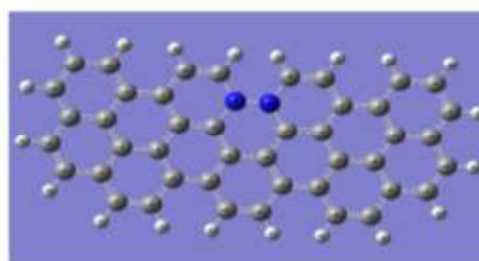
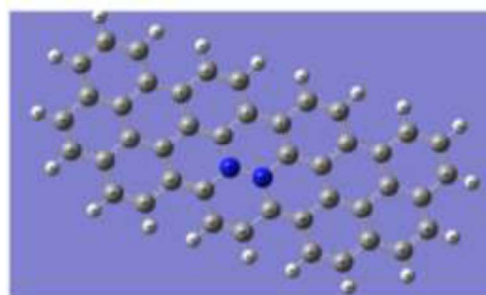
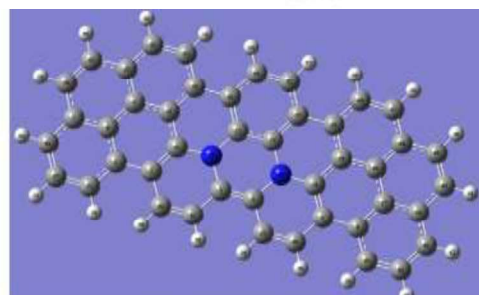
C <sub>46</sub> H <sub>20</sub>		C <sub>45</sub> NH <sub>20</sub>		C <sub>45</sub> NH <sub>18</sub>	
atom	Chemical shift	atom	Chemical shift	atom	Chemical shift
C8	118.04	C8	119.85	C8	119.88
C9	117.84	C9	119.90	C9	119.93
C10	117.55	C10	117.67	C10	122.02
C11	119.03	C11	122.05	C11	121.01
C12	118.77	C12	120.53	C12	122.08
C13	118.90	C13	125.74	C13	119.98
C14	118.92	C14	118.58	C14	120.00
C15	118.77	C15	121.32	C15	122.08
C16	119.03	C16	122.03	C16	121.01
C17	117.56	C17	119.71	C17	122.01
C18	117.84	C18	118.04	C18	119.93
C19	118.04	C19	117.77	C19	119.89
<sup>14</sup> N-NQCC(MHz)		<sup>14</sup> N-NQCC(MHz)		<sup>14</sup> N-NQCC(MHz)	
---		3.73		3.47	

The results show that in nitrogen containing graphene sheets, some calculated carbon chemical shifts are larger than that of graphene sheet. This indicates in N-graphenes, carbon atoms have a lower charge density and Conditions for oxygen attack have improved. Additionally, calculated NQCC of nitrogen atom in C<sub>45</sub>NH<sub>17</sub> is about 259KHz smaller than that of C<sub>45</sub>NH<sub>29</sub> and this indicates that nitrogen atom in C<sub>45</sub>NH<sub>17</sub> has more charge density than that of C<sub>45</sub>NH<sub>29</sub>. In other words, carbon atoms in C<sub>45</sub>NH<sub>17</sub> have lower charge density than C<sub>45</sub>NH<sub>29</sub> and therefore the presence of Nitrogen atom in graphene sheet, causes that charge density of carbon atoms decrease and Therefore, these atoms are more reactive in the four-electron path mechanism in the ORR reaction at the cathode.

The results of the table 2 show that:

- 1) The presence of two adjacent nitrogen atoms (Model I) has reduced the charge density of carbon atoms 10 and 13. The numerical increase in the amount of calculated chemical shifts of these atoms compared to previous models confirms this claim.
- 2) The presence of two nitrogen atoms in graphene according to model (II) has increased the charge density of middle carbon atoms. As can be seen, the average numerical value of the chemical shift of carbon atoms in this model is less than pure graphene. Increasing the charge density of carbon means that they are not a suitable target as the intermediate in 4-electron reaction of ORR, and the catalytic effect of this model will be less than that of pure graphene.
- 2) in the di-nitrogen (III) graphene model, carbon atoms have higher chemical shift values than pure graphene. This means that the carbon atoms in these models have a lower charge density than graphene, and the catalytic effect of these compounds is greater than that of pure graphene. In particular, carbon atoms 11 and

14 have the lowest charge densities and can be considered as the active site of the catalyst in ORR.

C<sub>44</sub>N<sub>2</sub>H<sub>20</sub>(I)C<sub>44</sub>N<sub>2</sub>H<sub>20</sub>(II)C<sub>44</sub>N<sub>2</sub>H<sub>20</sub>(III)

**Fig. 2.** Two nitrogen containing graphene sheets C<sub>44</sub>N<sub>2</sub>H<sub>20</sub> (I, II, III) considered in this study

**Table 1.** Calculated chemical shifts and nuclear quadrupole coupling constants of considered grapheme sheets

C <sub>44</sub> N <sub>2</sub> H <sub>20</sub> (I)		C <sub>44</sub> N <sub>2</sub> H <sub>20</sub> (II)		C <sub>44</sub> N <sub>2</sub> H <sub>20</sub> (III)	
atom	Chemical shift	atom	Chemical shift	atom	Chemical shift
C8	117.57	C8	123.30	C8	115.26
C9	122.45	C9	123.19	C9	117.72
C10	130.97	C10	107.27	C10	114.94
C11	125.55	C11	112.39	C11	128.40
C12	125.55	C12	113.63	C12	126.21
C13	130.97	C13	113.62	C13	126.21
C14	122.45	C14	112.39	C14	128.40
C15	117.57	C15	107.24	C15	114.94
C16	120.65	C16	123.19	C16	117.72
C17	118.64	C17	124.86	C17	115.25
C18	120.17	C18	113.60	C18	125.08
C19	117.57	C19	112.45	C19	115.43
<sup>14</sup> N-NQCC(MHz)		<sup>14</sup> N-NQCC(MHz)		<sup>14</sup> N-NQCC(MHz)	
4.43		4.26		4.48	

#### 4. CONCLUSION

According to the data obtained from charge distributions, it is concluded that:

- Calculated NMR and NQR parameters of nuclei can be used as a useful tool to understand the electronic structure of the compounds.
- The results show that in some nitrogen-containing graphene sheets (with one or two nitrogen), the effect of nitrogen atom on charge density of carbon atoms in the presence of nitrogen, charge density of some carbon atoms decreased and these atoms are better candidate as catalyst active site than pure grapheme.

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## محاسبات تئوری تابع چگالی برای بهبود کارایی پیل‌های سوختی در حضور ورقه‌های گرافن نیتروژن‌دار به عنوان کاتالیزور

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### چکیده

پیل‌های سوختی می‌توانند به طور مستقیم، با بازده بالا و بدون آلودگی انرژی شیمیایی را به انرژی الکتریکی تبدیل کنند. عوامل متعددی بر تبدیل انرژی شیمیایی به الکتریکی در پیل‌های سوختی موثر است که از آن جمله واکنش کاهش اکسیژن روی کاتد است. این واکنش یک فرآیند جنبشی کند است و بر عملکرد کلی یک پیل سوختی واکنش کاهش اکسیژن تاثیر دارد و از دو طریق ممکن است انجام شود: یکی مسیر مستقیم چهار الکترونی است که در آن  $O_2$  مستقیماً بدون دخالت پراکسید هیدروژن به آب کاهش می‌یابد. دیگری مسیر دو مرحله‌ای دو الکترونی است که در آن پراکسید هیدروژن به عنوان یک واسطه تشکیل می‌شود و با کاهش بازده پیل همراه است. برای دستیابی به یک پیل سوختی با بازده بالا، انجام واکنش کاهش اکسیژن از مسیر چهار الکترونی ارجح است. با توجه به اینکه فرآیند واکنش کاهش اکسیژن در طبیعت بسیار کند است، استفاده از کاتالیزورها جهت تسهیل مسیر چهار الکترونی و افزایش کارایی پیل‌های سوختی لازم است و پلاتین و آلیاژهای آن کاتالیزورهای معروفی در این زمینه اند که به علت قیمت بالا و نیز مسمومیت با CO، استفاده از آنها برای مصارف صنعتی به صرفه نیست. تحقیقات زیادی برای یافتن کاتالیزورهای مناسب به جای پلاتین و آلیاژهای آن در واکنش کاهش اکسیژن انجام شده است. در این تحقیق با استفاده از پارامترهای محاسبه‌شده NMR و NQR در برخی ورقه‌های گرافن حاوی نیتروژن (با یک یا دو نیتروژن)، تأثیر اتم نیتروژن بر چگالی بار اتم‌های کربن بررسی شد. نتایج نشان داد که در حضور نیتروژن، چگالی بار برخی از اتم‌های کربن کاهش می‌یابد و این اتم‌ها به‌عنوان جایگاه فعال کاتالیزور بهتر از گرافن خالص هستند.

### واژه‌های کلیدی

پیل‌های سوختی، صفحات گرافن نیتروژن‌دار، کاتالیزور، طیف سنجی NQR.