

Nanocatalyst FeN_4/C Molecular Orbital Behaviour for Oxygen Reduction Reaction (ORR) in Cathode Direct Methanol Fuel Cell (DMFC)

(Kelakuan Orbital Molekul Nanomangkin FeN_4/C untuk Tindak Balas Penurunan Oksigen (ORR) di Katod Sel Fuel Metanol Langsung (DMFC))

Sahriah Basri^a, Siti Kartom Kamarudin^{a,b}

^aFuel Cell Institute

^b Chemical Engineering Programme, Faculty of Engineering & Build Environment,
Universiti Kebangsaan Malaysia, Malaysia

ABSTRACT

Approaching commercialization phase of Direct methanol fuel cell (DMFC) technology, developing high kinetic rate active area with inexpensive non-precious metal catalyst (NPMC) for ORR catalyst materials to replace currently used Pt-based catalysts is a compulsory and crucial requirement in order to reduce the catalyst and overall system cost. Thus, the objective of this study is to describe the molecule orbital behavior of NPMC FeN_4/C and discuss of recent works in the area of non-precious metal electrocatalysts for ORR. Several important kinds of free energy study for carbon supported non-precious metal electrocatalysts for ORR by using density functional theory (DFT) in CASTEP module analysis. The properties of FeN_4/C nanocatalyst were studied, and their energy properties, band structure and density of state were evaluated accordingly. Besides, electronic properties of the nanostructure of FeN_4/C also calculated. The results indicated that optimized geometry shows the oxygen in 3.699 \AA from the catalyst opposite with the Fe atom. Moreover, HOMO occurs in the orbitals 173 and LUMO occur in orbitals 174 and the band gap -0.82 proved that FeN_4/C nanostructure catalyst is conductive and suitable to use as catalyst in fuel cell.

Keywords: Density functional theory; Non precious metal catalyst; Direct methanol fuel cell

ABSTRAK

Mendekati tahap pengkomersialan teknologi sel fuel metanol langsung (DMFC), membangunkan kawasan aktif dengan kadar kinetik yang tinggi dari pemangkin logam tidak berharga (NPMC) yang murah untuk mangkin ORR bagi menggantikan pemangkin berasaskan Pt yang sedia ada adalah keperluan wajib dan penting untuk mengurangkan pemangkin dan kos sistem keseluruhan. Oleh itu, objektif kajian ini adalah untuk menggambarkan kelakuan molekul orbital NPMC FeN_4/C dan membincangkan kerja-kerja baru-baru ini dalam bidang elektromangkin logam untuk ORR. Beberapa kajian tenaga bebas yang penting untuk karbon disokong elektromangkin logam berharga untuk ORR dengan menggunakan teori fungsi ketumpatan (DFT) dalam analisis modul CASTEP. Ciri-ciri nanomangkin FeN_4/C telah dikajii, dan sifat-sifat tenaga dan ketumpatan tenaga dinilai. Di samping itu, sifat elektronik nanostruktur FeN_4/C juga dikira. Keputusan menunjukkan bahawa geometri optimum bagi oksigen adalah pada jarak 3.699 \AA dari mangkin bertentangan dengan atom Fe. Selain itu, HOMO berlaku di orbital 173 dan LUMO berlaku di orbitals 174 dan jurang band -0.82 . Hal ini membuktikan bahawa pemangkin nanostruktur FeN_4/C adalah konduktif dan sesuai untuk digunakan sebagai pemangkin dalam sel fuel.

Kata kunci: Teori fungsian ketumpatan; Mangkin logam tidak berharga; Sel fuel methanol langsung

INTRODUCTION

Since 1960s, instability of NPMC in an acidic solution has been discovered. It is only has greatly improvement in recent years, but it is still not uncommon to have $\sim 20\%$ loss in performance during the first 2 h of operation (Lefevre et al. 2009). It was stated that a loss of $\sim 50 \text{ mV}$ was observed within only a few hours, followed by a more gradual but continuous loss of $\sim 5 \text{ mV/day}$ with no specific data was shown. It was ultimately culminating in a complete loss of catalyst activity (Alt et al. 1973). A conclusive description for this loss in performance was not provided, but several hypotheses were suggested. At least some of the decreasing in performance to oxidative

cross-linking of the macrocycles for the Co-based NPMCs (Alt et al. 1973) was recognized. Furthermore, Fe and Co-based NPMCs was initiated that for some of the metal centers which slowly leached out when soaked in H_2SO_4 , and as the temperature was increased from room temperature to 80°C the rate of metal leaching was greatly increased (Carmelo et al. 2018, Abdullah et al. 2004). It was also recommended that hydrogen peroxide, H_2O_2 which is generated during the ORR, may have oxidatively degraded the macrocycle, but it still have no supporting evidence was provided (Xin et al. 2017; Mohd et al. 2015).

Based on Banham et al. (2015) study, the poor in stability of NPMCs mechanism is not known with certainty, but the

main hypotheses are: 1) oxidative attack by H_2O_2 (or the resulting free radicals), 2) dissolution/leaching of the active metal site, and 3) protonation of the active site or protonation of a N species neighboring the active site followed by anion adsorption (Banham et al. 2015). It should be noted that, it is not possible nor should it be expected to clearly identify one single degradation mechanism for all NPMCs due to the variety of synthetic approaches and designs. While NPMCs have remarkably as a poor in stability (Dustin et al. 2015), it still has shown capable durability thru voltage cycling experiments because of the limited time spent in the potential region of 0.4-0.6 V. Otherwise, Jong & Chang (2017) study on nano-sized of graphene-based Fe/Co-N-C catalyst which is derived from the heat-treatment of a ball-milled graphene oxide. The developed catalyze ORRs at DMFC cathodes, exhibited a promising ORR activity and methanol-tolerance in the RDE-RRDE analyses, together with a dominant four-electron ORR selectivity. A mesoporous Fe-N-C catalyst was synthesized from glucose and ammonium hexacyanoferrate (II) hydrate by using NaCl as the template by Sa et al. (2018). In the presence of glucose, the NaCl-template was found to dominate the formation of the well-defined 3D hierarchical mesoporous structure with a high Brunauer-Emmett-Teller (BET) surface area (up to $911.56 \text{ m}^2 \cdot \text{g}^{-1}$), which can expose a large number of active sites for the ORR. However, even though it has a very outstanding methanol-tolerant property, the maximum power density at the optimized cathode compositions is still very low compared with that of Pt/C.

Thus, future work obviously needs to change the focus towards finding mitigations for the low stability of these catalysts since their activity is now satisfactorily high for many applications especially for low power applications such as distributed generation and backup power. The first strategy for preventing dissolution or leaching for acid wash the NPMC as a prior to use in the proton exchange membrane fuel cell (PEMFC) (Park et al. 2015). Conclusively, this strategy has been shown to be highly successful. However, due to oxidative attack by H_2O_2 and/or protonation of the active site much more limited success has been achieved in mitigating losses. It appears that these is still remaining as a challenges will have to be addressed through both activity and reactivity catalyst layer design approach. Finally, great attention and effort must have been taken when designing reactivity of NPMCs from Pt/C catalysts.

Many researchers try to use FeN_4/C or known as porphyrins as one of the chosen NPMCs catalyst (Akhbar 2018; Shou & Shih 2015; Xiaojuan et al. 2016). Porphyrins is a group of heterocyclic macrocycle organic compounds, composed with four modified pyrrole subunits which are interconnected at their carbon atoms via methane bridges ($=CH-$). The porphyrin is a group of porphyrin, substituted of porphines and also known as porphyrins. The non-nobel metal catalyst porphyrin ring structure is in group aromatic, with have total of 26 electrons in the conjugated system. In fact, various analyses showed that not all atoms of the ring are involved equally in the conjugation or based on several smaller conjugated systems, the molecule's overall nature

is substantially. Thus, this study focused on the density functional theory (DFT) study in molecular orbital behavior on the FeN_4/C nanocatalyst reactivity which is based structure of the Porphyrin and attached with 4 benzenes. It also calculates the band gap and energy properties of the structure after done geometry optimization. Besides, HOMO and LUMO of the catalyst to the oxygen investigates as follows the purpose on ORR in DMFC as selectivity of the geometry coordination in optimum structure.

COMPUTATIONAL METHOD

CASTEP in Accelrys Materials Studio (version 8.0) was used in this study. Calculations were performed based on density functional theory using a plane-wave basis set for expansion of the wave functions that were implemented using the CASTEP program. The DFT exchange-correlation potential for all calculations was based on the GGA-PBE functional with norm-conserving pseudopotentials. The plane-wave basis set was chosen with an equivalent energy cutoff of 430 eV. The bulk structure of FeN_4/C was first optimized. Then, the optimized structure was characterized with minimized energy. The structure of FeN_4/C was calculated using the GGA-PBE functional and the ultrasoft pseudopotential. Band structure, electron density and orbitals were chosen to run the jobs task. A negative adsorption energy indicates that the adsorption is stable (exothermic) with respect to the free gas phase adsorb.

RESULTS AND DISCUSSION

PROPERTIES OF FeN_4/C CATALYST

The properties of orbitals are presented in Table 1. It is observed that total number of valence orbitals is 752 and all the electron represent active at this structure. Thus, this prove that the structure in stable position and geometry. Figure. 1 shows the structure of FeN_4/C nanostructure catalyst with and without oxygen. In this study, the catalyst calculated for two optimized geometries, catalyst with oxygen and without oxygen as shown in Figure 1(a) and (b). The total number of atoms was 49 and 51 atoms, respectively.

TABLE 1. Properties of the structure

Properties of Orbitals	Number of electron
Total number of valence orbitals	752
Active electron number	346
Number of electron	346

Molecular modeling (MO) description of benzene, C_6H_6 , which is an aromatic hexagonal ring of six carbon atoms and three double bonds. In this molecule, 24 of the 30 total valence bonding electrons – 24 coming from carbon atoms and 6 coming from hydrogen atoms – are located in 12 σ (sigma) bonding orbitals, which are located mostly between

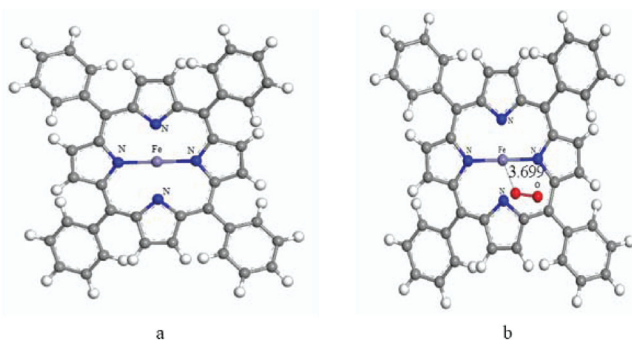


FIGURE 1. (a) FeN₄/C non precious metal catalyst structure, (b) FeN₄/C non precious metal catalyst with oxygen

pairs of atoms (C-C or C-H), similarly to the electrons in the valence bond description.

Figure 2 shows the oxygen position before and after geometry optimization. The optimized structure shows that gap 3.699 Å are the best geometry in minimizing the energy. At this distance, no chemical bonding are formed between catalysts and oxygen. To form bonding, the distance between the materials should be below 3 Å. Hence, at this distance, the physical bond formed where it is believed that the catalyst will help accelerate the reaction between oxygen and the proton for the ORR.

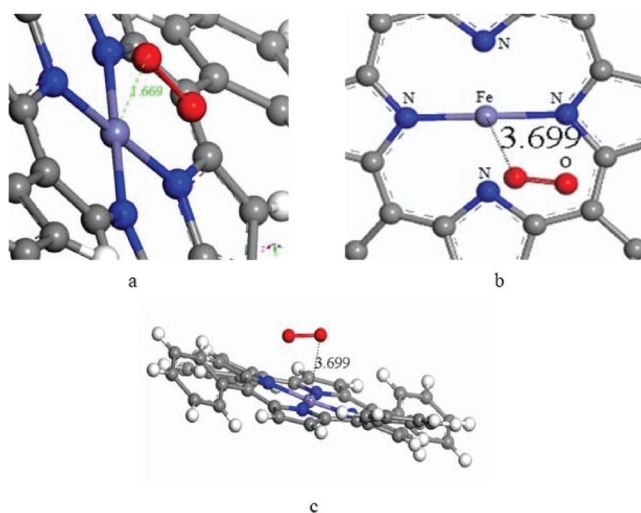


FIGURE 2. (a) Oxygen position before geometry optimization, (b) Oxygen position after geometry optimization (b) Oxygen position after geometry optimization (side view)

BAND STRUCTURE AND DENSITY OF STATE

To visualize the difference between conductors, insulators or semiconductors is to plot the available energies for electrons in the materials. Instead of having discrete energies as in the case of free atoms, the available energy states form bands. In order to know the conduction process is whether or not there are electrons in the conduction band. Otherwise, in insulators the electrons in the valence band are separated by a large gap from the conduction band, in conductors like metals the valence band overlaps the conduction band, and in semiconductors there is a small enough gap between

the valence and conduction bands that thermal or other excitations can bridge the gap. With such a small gap, the presence of a small percentage of a doping material can increase conductivity dramatically. It can be observing by defined the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO). An important parameter in the band theory is the Fermi level, the top of the available electron energy levels at low temperatures. The position of the Fermi level with the relation to the conduction band is a crucial factor in determining electrical properties.

Table 2 shows the properties of HOMO and LUMO in terms of the orbital number and energy around the FeN₄/C catalyst. HOMO occurs in the orbitals 173 and LUMO occur in orbitals 174. The gap between HOMO and LUMO are called band gap. It value is indicated of the material properties in terms of conductivity due to the electron and free electron activity. Band gap -0.82 eV indicate that FeN₄/C nanostructure catalyst is slightly conductive and suitable to use as cathode catalyst for ORR in fuel cell system. The electronic properties of the bare catalyst alloy are derived from DFT calculations, and the results provide the energy gaps between the HOMO and LUMO, which are related to the stability of the FeN₄/C nanocatalyst. Hence, it proves that band gap of 0.82 eV shows the stability of FeN₄/C is substantially higher. This enhanced stability may be responsible for the increased durability of the FeN₄/C catalyst in comparison to Fe in fuel cells (Jing et al. 2014). Negative sign of energy shows that the reaction occurs is an exothermic reaction.

TABLE 2. Band structure

Energy properties	Band Structure	
	Orbital number	Energy (eV)
HOMO	173	-4.90
LUMO)	174	-4.08
Band gap		0.82

Figure 3(a) and (b) shows the active electron gathered on the Fe and N atoms at HOMO of the FeN₄/C catalyst without oxygen. While, Figure 3(c) and (d) shows the HOMO and LUMO of catalyst with the oxygen. It can be observing that; HOMO occurs in most atoms but not in Fe atom while LUMO occur in Fe atom. In this condition will helps in reaction where electron easily transfers from N to Fe. Furthermore, with the presence of oxygen, more electrons are exposed to oxygen. This is the evidence of the kinetic energy increase with the presence of the oxygen at the catalyst FeN₄/C. It will increase the ORR reaction rate for oxygen with electron and proton in the cathode side layer.

In benzene, the remaining six bonding electrons are located in three π (pi) molecular bonding orbitals that are delocalized around the ring. Two of these electrons are in an MO that has equal orbital contributions from all six atoms. The other four electrons are in orbitals with vertical nodes at right angles to each other. As in the valence bond theory, all of these six delocalized π electrons reside in a larger space

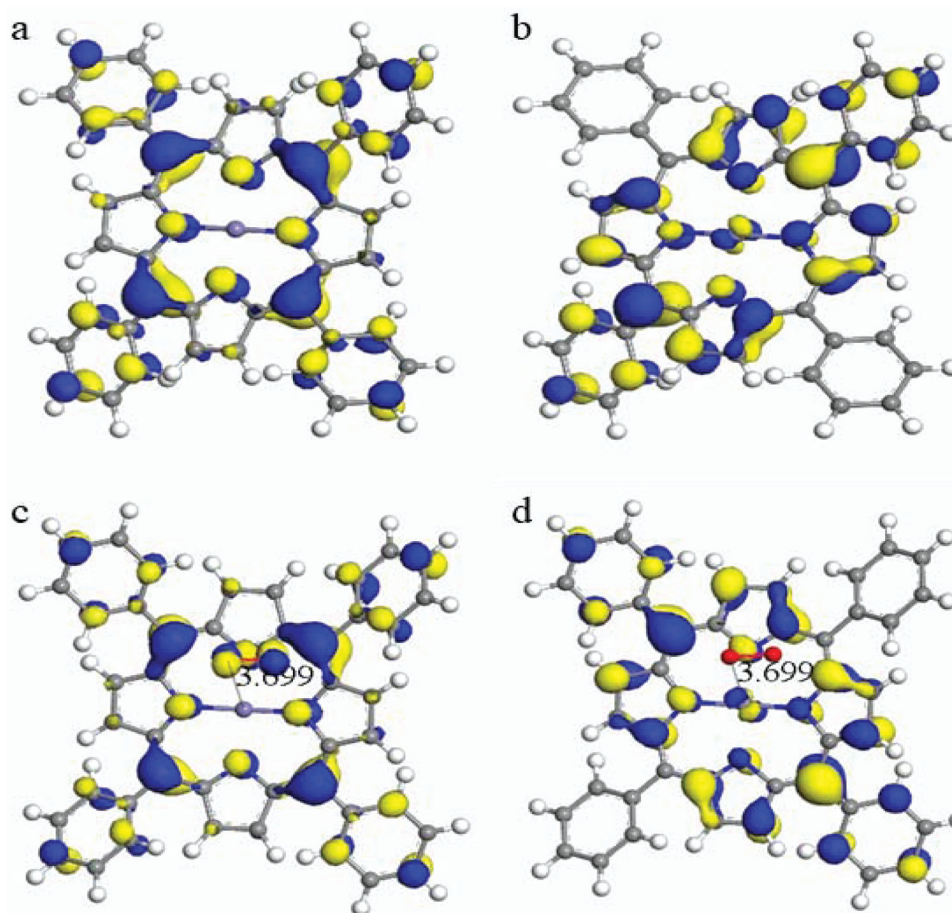


FIGURE 3. (a) HOMO and (b) LUMO for nanocatalyst structure without oxygen, (c) HOMO and (d) LUMO with oxygen

that exists above and below the ring plane. All carbon-carbon bonds in benzene are chemically equivalent. In MO theory this is a direct consequence of the fact that the three molecular π orbitals combine and evenly spread the extra six electrons over six carbon atoms.

Figure 4 shows the total density of the catalyst which is electron in high density around the catalyst is equivalent and uneven distribution. This state is very important characterization for fuel cell catalyst to increase the reaction rate and also conductivity of the layer.

To further understand the catalytic activity at the microscopic level, the FeN_4/C clusters with adsorbed reactants are constructed, and the resulting electronic parameters are extracted from DFT calculations. These results indicated that FeN_4/C not only can feasibly be used for electrocatalytic reactions but is also a promising system for the exploration of the sensitivity of reaction geometries, thermodynamics and potentially kinetics to the electrochemical environment, thereby providing a framework for the determination of potential-dependent redox reaction energy paths. Throughout this study, a nanocatalyst FeN_4/C constructed from 50 atoms then run geometry optimization before energy optimization.

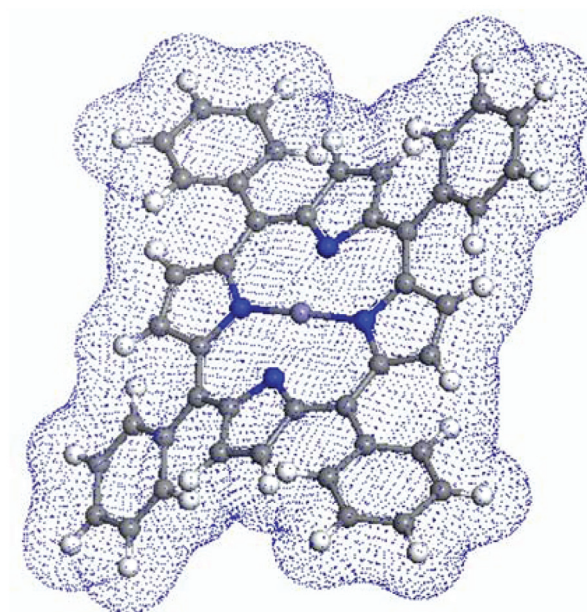


FIGURE 4. Total density of state simulation of FeN_4/C nanocatalyst

Table 3 shows the energy properties for the oxygen reduction reaction (ORR) on FeN_4/C , NPMCs nanocatalyst. The atomic energy of FeN_4/C is very exothermic, with a value of -85,942.51 eV, which indicates that FeN_4/C is stable. While binding energy is 410.87 eV. The favorable binding of the catalyst can change the electrical properties of the catalyst, which explains the observed increase in the conductivity after oxygen adsorption on the catalyst layer. The reason for the high electron transfer is due to the stronger interaction between the FeN_4/C and O_2 in the latter, which is further diminished by the adsorbed oxygen. Furthermore, the energy gap for FeN_4/C is also small and suggesting that it is a conductive material.

TABLE 3. Energy properties for the oxygen reduction reaction (ORR) on FeN_4/C

Energy Components	Energy (eV)
Sum of atomic energies	-85,942.51
Binding energy	-410.87
Kinetic	-369.78
Electrostatic	-283.26
Exchange-correlation	138.50
Spin polarization	103.67

The kinetics energy of -369.78 eV shows that FeN_4/C have high exothermic kinetic of the atom. It is equal to 5.92×10^{-17} Joule. Thus, FeN_4/C has high reaction activation energy which helps in ORR to produce water in cathode catalyst layer. This results is comparative with Feng et al. (2015). Other energy properties such as electrostatic, exchange correlation, spin polarization and binding energy relatively stable. Electrostatic potential energy, is a potential energy that results from conservative Coulomb forces and is associated with the configuration of a particular set of point charges within a defined molecular system. A molecule may have electric potential energy by virtue of two key elements: its own electric charge and its relative position to other electrically charged molecule. In this case, it refers to the relation between Fe catalyst and the oxygen molecules. High electron density area as discussed above contributes to the low exchange correlation energy. While spin polarization associated with conduction electrons in metals like Fe that led to the current spin polarization.

CONCLUSION

The reactivity of non-precious metal nanocatalyst FeN_4/C described in this study with focus on molecular orbital behavior including band gap, electron density and energy properties. The optimized geometry shows the oxygen in 3.699 \AA from the catalyst opposite with the Fe atom. The calculated band gap for NPMC nanocatalyst FeN_4/C is much lower of 0.82 eV and can be overcome using hybrid density functional theory. The calculated band gaps shows eventually reaching that of as an oxygen-reduction catalyst element

because they show negative adsorption energy. Presence of oxygen in the catalyst shows increase the density of the electron in catalyst. Certainly it will increase the ORR reaction rate for oxygen with electron and proton in the cathode side layer. Besides, the binding energy of FeN_4/C is very exothermic, with a value of -85,942.51 eV, which indicates that FeN_4/C is stable. Therefore, FeN_4/C has potential to be implemented as catalyst support in the cathode of a DMFC.

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*Sahriah Basri
Fuel Cell Institute,
Universiti Kebangsaan Malaysia,
Bangi, Malaysia.

Siti Kartom Kamarudin
Fuel Cell Institute,
Universiti Kebangsaan Malaysia, Malaysia,
Chemical Engineering Programme,
Faculty of Engineering & Build Environment,
Universiti Kebangsaan Malaysia, Malaysia

*Corresponding author;
email: sahriah@ukm.edu.my

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