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# Novel cathode catalyst for DMFC: Study of the density of states of oxygen adsorption using density functional theory

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## ABSTRACT

Platinum (Pt) is the most common cathode catalyst in Direct Methanol Fuel Cells (DMFC). However, Pt involved both in the oxidation reaction of methanol and the reduction of oxygen on the cathode side, which limits the performance of DMFCs. Therefore, this study investigates cobalt phthalocyanine (CoPc) as a potential DMFC cathode catalyst capable of inhibiting the reactivity of methanol oxidation. This study investigates the reaction mechanism and adsorption energy of oxygen molecules on Cobalt Phthalocyanine (CoPc) using the Density Functional Theory (DFT). The basis sets of semi-core pseudopotential (DSPP) and effective core potential are used to compare the geometric optimization of the Cobalt Phthalocyanine structure. The adsorption strength of molecular oxygen on the Cobalt metal center of Phthalocyanine is investigated using Partial Density of States and compared with that of Iron Phthalocyanine (FePc). Finally, the results show that the adsorption energy of carbon monoxide and methanol on the Cobalt and Iron metal centers of the Phthalocyanine complex yield low energy adsorption on CoPc. It was observed that the adsorption energy when two metal sites of CoPc and supported CoPc on tungsten atom are involved yields high energy adsorption and bond length of molecular oxygen that would lead to oxygen bond dissociation. Therefore, this study concludes that CoPc has the potential to replace Pt due to its high tolerance to methanol and carbon monoxide oxidation.

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## Introduction

Fuel cells that convert chemical energy to electricity have a great potential to replace fossil fuels. Direct methanol fuel

cells (DMFCs) that use methanol as a fuel to produce electricity represent a promising technology that has the advantages of low emissions of carbon dioxide, high power density and high energy density [1,2]. Despite these advantages, many

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obstacles must be overcome to make commercialized DMFCs, such as replacing the platinum cathode catalyst [3].

The reaction at the cathode side is the reduction of oxygen to produce water. The commercially used cathode catalyst for DMFCs is currently a platinum catalyst. By using a platinum catalyst, the rate of conversion to produce water is low because platinum also reacts with methanol and methanol crossover from the anode forms carbon dioxide [4]. The competing reactions of methanol oxidation and oxygen reduction at the cathode side lower the potential performance of DMFCs [5]. This obstacle can be overcome by replacing platinum with a catalyst that has little or no oxidative reaction with methanol [6,7]. Using a platinum catalyst also increases the cost of production, thus hindering commercialization [8].

Many studies have attempted to replace the platinum catalyst at the DMFC cathode side [8] or to alloy Platinum with another metal, for example, chalcogenides [9–11], palladium [12] and others [5,13–18]. Transition metal- $N_4$  macrocycles have attracted much attention as an alternative to precious metals as cathode catalysts for oxygen reduction in DMFCs. Potential transition metal- $N_4$  macrocycles include metal phthalocyanine, metal porphyrin, metal tetraphenylporphyrin, metal octaethylporphyrin and others [19–26]. Transition metal- $N_4$  macrocycles have lower costs compared to other metals and a high methanol tolerance, which are advantages in their use as cathode catalysts in DMFCs [6,27,28].

All of these transition metal macrocycles have activity and selectivity toward the oxygen reduction reaction (ORR), but the mechanism responsible for the ORR activity is not clearly understood [29]. The three adsorption models for molecular oxygen are the Griffiths model, Pauling Model and Yeager Model [30]. The Pauling model is the appropriate adsorption model for transition metal macrocycles because there is only one transition metal at the center of their structures. Several studies have investigated the adsorption of oxygen molecules on Cobalt Phthalocyanine (CoPc), such as the work performed by Shi et al. [31] in which both end-on and side-on binding sites of oxygen molecule adsorption were studied. They proved that Cobalt Porphyrin (CoP) derivatives have a higher ionization potential than Iron Porphyrin (FeP) derivatives however, Iron Phthalocyanine (FePc) derivatives have a higher ionization potential than Cobalt Phthalocyanine (CoPc) [31]. Wang et al. [32] published a DFT-based study on the adsorption of oxygen molecules on FePc and CoPc in both end-on and side-on configurations and found that CoPc is stable with the end-on configuration of oxygen adsorption but FePc is stable in both configurations. The end-on configuration leads to the formation of Hydrogen peroxide ( $H_2O_2$ ) by CoPc and water by FePc. He et al. [33] studied oxygen molecule adsorption on FePc, CoPc, FeP and CoP and found that FePc and FeP reduced the oxygen molecule to water, while CoPc and CoP reduced the oxygen to hydrogen peroxide because the Iron metal center has a higher oxygen reduction ability than the Cobalt metal center.

He et al. [33] studied the adsorption of  $O_2$ , OH and  $H_2O_2$  molecules on Transition Metal (TM) macrocycles, including TM Porphyrins, TM Tetraphenylporphyrins, TM phthalocyanines, TM fluorinated phthalocyanines and TM chlorinated Phthalocyanine, where the TMs used were Cobalt and Iron. The adsorption energy of the OH molecule is lower on FePc

compared to CoPc, which leads to stronger binding between OH and the iron metal center. This effect of FePc can be used to reduce oxygen in an alkaline medium. Orellana [34] studied oxygen adsorption on CoPc-functionalized single-walled carbon nanotubes and found that the  $sp^2$ -like bonds of functionalized CNTs have strong reduction abilities. Khanfar and Morin [35] examined a modified monolayer of CoPc and presented scanning tunneling microscopy (STM) results that showed a frontier orbital electron density similar to that calculated via DFT.

However, there is no detail study reported on the strength of bonding between oxygen and CoPc via density states of oxygen adsorption. Therefore, the main objective of this paper is to study the adsorption energy of the oxygen molecule and hydrogen atom to Cobalt Phthalocyanine (CoPc) through the d-band model theory of Partial density of states (PDOS). The PDOS of CoPc complex is compared with the FePc complex. Moreover, this study also explores further a possible reaction pathway of the oxygen reduction reaction that could produce water as product. More pathways will also be introduced to demonstrate the interaction between adsorbate and CoPc as well as its limitations. This study also examines the adsorption of methanol and carbon monoxide on CoPc. The oxygen adsorption on two sites of the Cobalt metal center of Phthalocyanine and supported CoPc on tungsten atom also has been studied. The strength of adsorption is determined by density of states.

## Computational method

The program Materials Studio DMol3 (version 5.5) from Accelrys is used in this study. Density functional theory (DFT) calculations were carried out with the PBE functional. Effective potential with relativistic effect-accounted DFT semi-core DSPP and effective core potential (ECP) were applied for optimization of the Cobalt Phthalocyanine structure. The ECP was applied to all calculations, except for the two-site calculation at the Cobalt metal center of Phthalocyanine, for which DSPP was used. DNPs, double numerical plus polarization function basis sets, were employed for all the calculations. The spin unrestricted method was used for all open shell systems. The SCF criterion used was  $10^{-6}$  Hartree for the total energy. All structures were fully optimized without any symmetry constraints, with a convergence criterion of  $0.004 \text{ Ha } \text{\AA}^{-1}$  for the forces,  $0.005 \text{ \AA}$  for the displacement and  $2 \times 10^{-5} \text{ Ha}$  for the energy change. The adsorption energy is calculated as  $E_{\text{ads}} = E_{\text{substrate+adsorbate}} - E_{\text{substrate}} - E_{\text{adsorbate}}$ , where  $E_{\text{substrate+adsorbate}}$ ,  $E_{\text{substrate}}$ , and  $E_{\text{adsorbate}}$  refer to the total energies of a substrate and adsorbate, a substrate and a gas phase adsorbate, respectively. A negative adsorption energy indicates that the adsorption is stable (exothermic) with respect to the free gas phase adsorbate. The free energy for all reactions is calculated by using reaction (1) to form the free energy diagram for all oxygen reduction paths, where  $\Delta E$  is the total energy taking from the DFT calculation, ZPE is the zero point energy,  $T$  is the temperature and  $S$  is the entropy.

$$\Delta G = \Delta E + \Delta ZPE - T\Delta S \quad (1)$$

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