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# Metallomacrocyclic–carbon complex: A study of bifunctional electrocatalytic activity for oxygen reduction and oxygen evolution reactions and their lithium-oxygen battery applications

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## ABSTRACT

A metallophthalocyanine – carbon complex is designed by a simple approach to achieve superior, bifunctional catalytic activity. A simple and cost-effective technique is utilized to prepare carbon_iron phthalocyanine composites. Furthermore, to investigate ball milling effects, iron phthalocyanine is ball milled, which is used to prepare the carbon_ball-milled iron phthalocyanine composites. All the prepared composites exhibit better catalytic activity in both oxygen reduction and oxygen evolution reactions than Pt/C, indicating carbon support significantly improves the stability, conductivity, and surface properties of iron phthalocyanine. The ball-milling improves specific surface area, which in turn enhances the oxygen evolution reaction activity of the composites. When the carbon-iron phthalocyanine composites were applied to an air-cathode catalyst in a lithium-oxygen battery, high reversibility and low over-potential were attained. Among all the synthesized catalysts, the reduced graphene oxide_ball-milled iron phthalocyanine composite exhibits superior bifunctional electrocatalytic activity with high reversibility (92%) and low over-potential (0.7 V) due to enhanced surface properties.

## 1. Introduction

The rechargeable lithium-oxygen ($Li\text{-}O_2$) battery is an attractive candidate for the next generation energy storage devices due to their high theoretical specific energy (11,425 Wh/kg) [1]. However, there are still various critical issues to overcome in order to make them practical. Particularly, the development of effective bifunctional electrocatalysts is of crucial importance in order to achieve high efficiency and long cycle life. A bifunctional catalyst should catalyze both oxygen reduction reactions (ORR) and oxygen evolution reactions (OER) that take place in the $Li\text{-}O_2$ battery. During the early stage of catalyst development, various ORR catalysts have been successfully reported [2–4] whereas the development of OER catalysts is still behind. An OER catalyst should effectively decompose the solid discharge product ($Li_2O_2$) at a low over-potential. So far, a great deal of attention has been paid to the development of such bifunctional catalysts, which include carbons, oxides, carbides, nitrogen doped carbons and perovskites, but the low over-potential criterion is yet to be satisfied [5–8]. Hence it is necessary to develop a suitable bifunctional catalyst that catalyzes the OER, as much as the ORR activity that takes place in the $Li\text{-}O_2$ system.

Among the various non-precious catalysts that are being investigated, phthalocyanine (Pc) has attracted enormous interest due to its low cost, outstanding electronic properties, and facile preparation methods [9–15]. Especially, metal phthalocyanine is capable of reducing oxygen at higher potentials and is considered the most suitable ORR catalyst [16]. Electrocatalytic studies on the ORR performance of the metal phthalocyanine have been reported over the years [16–19]. However, the poor electron conductivity and stability of phthalocyanine complexes makes them inadequate for practical applications. To overcome these issues and to enhance their ORR performance, various possible approaches are adopted, like the incorporation of nitrogen coordinates, transition metal supports, pyrolysis treatment and carbon supports. Among them, employing a suitable carbon support is considered to be a simple and cost-effective method [17,20–23]. Carbon-supported metal phthalocyanine has been verified to improve conductivity and stability, and greatly enhance ORR activity [23–26].

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Recently, Li et al. [27] studied the ORR performance of three different types of carbon-supported phthalocyanine for fuel cells and observed excellent stability compared to commercial Pt/C. Metal phthalocyanine has been employed in various carbon supports including Vulcan carbon, ordered mesoporous carbon, graphene sheets and mesoporous carbon vesicles for various applications [27–29]. However, the synthetic methods require tedious experiments that are hard to tailor to structure and surface properties. The preparation methods also involve expensive processes, since phthalocyanine is poorly dispersed in many solvents, complicating overall synthesis.

Metal phthalocyanine as an OER catalyst has received much less attention. Abbaspour et al. [30] attempted to improve OER activity with phthalocyanine-multi-wall carbon nanotube (MWCNT) complexes in acidic and alkaline media. However, according to previous studies, the lack of proper interface between phthalocyanine and carbon makes them poor OER catalysts [27]. So, enhancement of OER activity by metal phthalocyanine remains undeveloped.

Similarly, in terms of lithium-air battery application, very few studies have been reported for phthalocyanine. In fact, phthalocyanine has been employed as a redox mediator in the electrolytes as a solution phase catalyst [22]. Only recently, Trahan et al. [31] reported cobalt phthalocyanine (CoPc) was a suitable ORR catalyst for lithium air batteries and explained the discharge chemistry of CoPc in the air-cathode. Other than that, to the best of our knowledge, utilization of phthalocyanine as a solid bifunctional (both ORR and OER) catalyst for lithium-air batteries has not been reported.

Therefore, even though phthalocyanine has been examined as a catalyst for a period of time, it still needs further detailed investigations in various areas. It is necessary to develop a facile and simple way to prepare carbon-supported metal phthalocyanine with improved ORR performance. It is also essential to find a simple and efficient way to improve the interface state between phthalocyanine and carbon and thereby to enhance their OER activity. At the same time, application studies of the metallophthalocyanine–carbon complex as bifunctional electrocatalysts in the Li-$O_2$ battery are needed to enhance battery efficiency.

In our previous work [32], we developed iron phthalocyanine (FePc) supported with graphite nanofibers (GNF) to form mesoporous cathode catalysts. The synthesized electrocatalysts showed good surface properties, electrocatalytic activities and proved to be potential electrocatalysts for Li–$O_2$ batteries. The results were published without further delay. However, to further extensively investigate this combination, to understand the relation between the metal phthalocyanine and the carbon support, and to improve the bifunctional catalytic activity (mainly OER), further studies presented in this work.

In this work, the bifunctional electrocatalytic activity of iron phthalocyanine (FePc) anchored on two different carbon supports (reduced graphene oxide [RGO] and carbon nanotube [CNT]) are extensively studied. A simple and cost-effective technique is used to prepare the RGO_FePc and CNT_FePc composites. Moreover, to enhance the OER characteristics by improving the interface between the phthalocyanine and carbon, surface properties of Pc are enhanced by ball-milling (BM). That is, FePc was ball-milled and the RGO_BM FePc and CNT_BM FePc composites are prepared in the same way. Ball-milling significantly reduced the particle size of FePc and improved the overall surface area of the composites. The electrocatalytic activity of both ball-milled (RGO_BM FePc and CNT_BM FePc) and non-milled (RGO_FePc and CNT_FePc) composites are comparatively analyzed in both aqueous and non-aqueous media. The experimental results suggest that it is possible to improve the OER activity of the carbon_FePc composites by improving their surface characteristics. Also, when applied in the non-aqueous lithium-oxygen battery system, carbon_FePc composites delivered high specific capacity and low over-potential, exhibiting improved ORR and OER activities.

## 2. Materials and methods

### 2.1. Preparation of carbon–metal phthalocyanine composites

Iron phthalocyanine (FePc, 90% purity) was commercially purchased from Sigma-Aldrich (USA) and used without further purification. Reduced graphene oxide (RGO) and carbon nanotube (CNT) were commercially purchased (Carbon Nanomaterial Technology, Co., Ltd. South Korea) and treated with 96.8 ml sulfuric acid of 98% purity and 42 ml nitric acid of 63% purity before any further processing. Carbon_FePc composite was prepared by a simple 3 step process. An equal amount (40 mg) of FePc and carbon (RGO, CNT) was dispersed in 100 ml dimethyl formamide (DMF) separately and then they were mixed together drop-wise. The mixed solution was stirred for 7 h at room temperature and ultrasonicated for 40 mins. Then the obtained carbon_FePc composites were washed with DMF and vacuum dried at 80 °C. To evaluate the effect of ball milling, a portion of FePc was ball-milled (BM) at the sample-ball ratio of 1:50 in a ball miller reactor at 250 rpm for 1 h. Carbon_BM FePc composites were also prepared by the three step process mentioned above. The as-prepared composites are named (i) RGO_FePc, (ii) RGO_BM FePc, (iii) CNT_FePc, and (iv) CNT_BM FePc.

All the material characterization techniques utilized in this study are explained in detail in the supporting information. The electrocatalytic activity of the sample was evaluated in both aqueous and non-aqueous media. A detailed description of the electrochemical characterization techniques used is also given in the supporting information.

## 3. Results

### 3.1. Physical characterisation

The structural characteristics of synthesized composites are examined by X-ray diffraction as given in Fig. 1(a). The sharp peaks at 7.0, 9.2, 18.2, 18.6, 23.9, 26, 28, 29.6, 30.6° are well indexed to characteristic FePc planes (110), (102), (302), (104), (105), (401), (314), (215), (315), respectively [JCPDS No.14-0926] [20]. After ball milling, however, the FePc diffraction peaks are much lower in intensity and form few broad peaks at 7.2° and between 22 and 27° respectively, as reported in the literature [21]. The broadening of the XRD peaks reveals the loss of FePc crystallinity due to severe plastic deformation induced by high energy ball impacts [22]. No new peak is found in the pattern, indicating that no new structure is formed during milling. CNT exhibits diffraction peaks at $2\theta = 26$ and 43°, which correspond to the graphitic planes of (002) and (100) [23]. RGO shows a broad peak between $2\theta = 22$ and 25° that corresponds to the graphitic (002) plane [24]. The synthesized composites such as RGO_FePc and CNT_FePc possess both the characteristic peaks of phthalocyanine and carbon with a slight peak position shift. A similar observation is also seen for RGO_BM FePc and CNT_BM FePc, with low-intensity diffraction peaks, as seen from the ball milled FePc. The inclusion of both the characteristic peaks is notable evidence for the proper formation of carbon_FePc composites without any other impurities. The peak position shift indicates the occurrence of monomeric FePc that are attached to carbon crystals [33]. The pristine FePc exhibits a peak at 7° that usually appears due to molecular aggregation. However, the broadening of the peak at 7° observed in the as-prepared composites discloses that FePc molecules on carbon are less aggregated [34]. The particle size of FePc was calculated by the Debye-Scherrer equation (Eq. (1)) from the XRD patterns [35].

$$D = 0.9\frac{\lambda}{d\cos\theta}, \tag{1}$$

where $\lambda$ = wavelength, d = the full width at half maximum intensity of the peak, and $\theta$ = diffraction angle. The particle size of FePc in