



## Cobalt Phthalocyanine Catalyzed Lithium-Air Batteries

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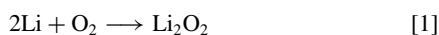
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The full reduction of O<sub>2</sub> to Li<sub>2</sub>O is the ultimate chemistry desired for building a super high energy density Li-air battery. Most investigations to date have identified Li<sub>2</sub>O<sub>2</sub> as the discharge product which limits the specific energy of the Li-air battery to 3500 Wh kg<sup>-1</sup>, about 67% of the theoretical value. Here, for the first time, we report the full reduction of O<sub>2</sub> to Li<sub>2</sub>O in a Li-air cell using cobalt phthalocyanine catalyzed carbon cathodes. Details of the oxygen reduction reaction mechanism have been discerned through cyclic voltammetry experiments in half cells as well as analysis of discharged Li-air cell cathodes by means of X-ray absorption spectroscopy and X-ray diffraction. The catalyst lowers the activation energy for O<sub>2</sub> reduction by forming a complex with superoxide, and enables the reduction of Li<sub>2</sub>O<sub>2</sub> to Li<sub>2</sub>O. In addition, the catalyst is effective in lowering the gap between the discharge and charge voltage plateaus leading to an increase in the energy efficiency of the Li-air battery. The breakthrough in the discharge chemistry being reported could lead to the realization of the full potential of the Li-air battery.  
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The battery based on the lithium metal anode (negative electrode) and oxygen cathode (positive electrode), generally known as the Li-air battery since oxygen is accessed from the air in the atmosphere, is perhaps the highest energy density, low cost, battery that is practically possible.<sup>1-4</sup> Our recent investigations of oxygen reduction reactions (ORR) in non-aqueous electrolytes have revealed that the reduction mechanism is influenced by the Lewis acidity of the cation of the supporting electrolyte (ion-conducting electrolyte salt) and the donor number (DN) (or the Lewis basicity) of the solvent medium.<sup>1-4</sup> The overall reaction in a Li/O<sub>2</sub> battery cell is now recognized to be the two-electron process shown in equation 1 below. The four-electron reduction of O<sub>2</sub> converting it to Li<sub>2</sub>O as depicted in equation 2 is not generally achieved in Li-O<sub>2</sub> battery cells due to kinetic factors.<sup>5</sup>



The theoretical specific energy of the Li-air battery with the discharge reaction shown in equation 1 is 3505 Wh kg<sup>-1</sup>, which is 33% less than when the reaction is that displayed in equation 2 with a specific energy of 5200 Wh kg<sup>-1</sup>. It is believed that the use of appropriate catalysts in the carbon cathodes of Li-air cells could promote full reduction of O<sub>2</sub> to Li<sub>2</sub>O, although most of the studies reported to date utilizing a variety of catalysts have not demonstrated the cell discharge reaction depicted in equation 2.<sup>6-22</sup> An effective ORR catalyst will also lower the activation energy for O<sub>2</sub> reduction and raise the load voltage of the Li-air cell, thereby contributing to an additional increase in the practical energy density of Li-air batteries. A review of catalysis in non-aqueous Li/O<sub>2</sub> battery was recently published.<sup>23</sup>

Cobalt phthalocyanine (CoPC) has been investigated as a non-precious metal catalyst for the ORR in aqueous PEM fuel cells.<sup>24-29</sup> These investigations show that heat-treatment of the CoPC-containing carbon yields a catalytically active electrode material in both alkaline and acidic electrolyte environments. In their original work on the non-aqueous Li-air battery, Abraham et al showed<sup>4</sup> that a catalyzed cathode composed of carbon black and CoPC pyrolyzed at temperatures between 600 and 800°C exhibited catalytic activity for the oxygen reduction reaction, manifested as an increase in the discharge load voltage of the Li-air cell and improved rechargeability of the discharged cell. Mechanistic details of the observed ORR catalysis by CoPC in the non-aqueous Li-air cell have not yet been studied and are the focus of this work.

Here, we report on the preparation and characterization of the CoPC-containing carbon black electrode which results upon pyrolysis of the carbon black/CoPC mixture at 600°C, referred to as Co600 electrode throughout this paper. A detailed understanding of the changes in oxygen reduction reactivity brought forth by the Co600 reaction center in the porous carbon electrode is obtained from O<sub>2</sub> half-cell voltammetry in conjunction with the X-ray Absorption Spectroscopy (XAS), and X-ray diffraction (XRD), and Scanning Electron Microscopy (SEM) analysis of discharged Li-O<sub>2</sub> cell cathodes.

It is shown that the rate-determining step in the ORR of CoPC catalyzed Li-air cell is the formation of the catalyst-stabilized superoxide, O<sub>2</sub><sup>-</sup> formed from the one electron reduction of oxygen. The stabilization of O<sub>2</sub><sup>-</sup> by the CoPC catalyst lowers the activation energy for O<sub>2</sub> reduction and increases the load voltage of the cell. The X-ray diffraction data obtained from discharged cathodes of Li-O<sub>2</sub> cells show that the catalyst also promotes the full reduction of O<sub>2</sub> to O<sub>2</sub><sup>2-</sup>, and improves the rechargeability of the Li-air battery as demonstrated by lower charging voltage. These results are reported here.

### Experimental

*Preparation of Co-catalyzed high surface area carbon powders.*— Carbon black samples containing Cobalt catalyst were prepared as previously described.<sup>27</sup> Briefly purum grade cobalt phthalocyanine as received from SigmaAldrich was dissolved in a concentrated sulfuric acid solution after which carbon black was added under stirring until a homogenous paste was formed. The mass of the high surface area carbon added was set so that the solid phase of the slurry contained 2 wt% cobalt metal. The paste was then instantaneously diluted via directly transferring into a large volume of deionized water forcing CoPC to precipitate out of solution and deposit onto the carbon black. Aliquots of the Co600 catalyst powder were separately synthesized with both the Vulcan XC72R and Ketjen300 carbon black powders. The particulate suspension was then separated via vacuum filtration and the resulting powder was dried under vacuum at 70°C. Dried powder samples were then loaded into an argon purged quartz furnace tube and sintered at 600 Celsius for four hours.

*Preparation of dispersions for thin film analysis.*— High surface area carbon ink suspensions for thin film voltammetry experiments were created by dissolving a polyvinylidene fluoride (PVDF) Kynar 2801 binder material into a N-methyl-2-pyrrolidone solvent. Catalyzed or uncatalyzed carbon powder was then added (90:10 powder:binder by mass) to the binder solution and sonicated until a homogenous ink suspension resulted. Microliter aliquots of the ink suspension were cured onto a 0.196 cm<sup>2</sup> glassy carbon working electrode substrate at 80°C under vacuum creating carbon/catalysts films of 100 μg cm<sup>-2</sup>.

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