Nanocatalysts in Lithium Oxygen Batteries

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Lithium ion batteries are currently used in several areas of technology, including transport, portable electronics, medical devices, power tools, and storage of electricity produced by renewable sources like solar, wind, etc. With the increasing demand and usage of high-performance batteries in hybrid and electric cars, and more demanding electronic gadgets, the physical limits of the materials used in batteries are being tested. While these batteries deliver high energy density, they have limited cycle life and power density. Lithium oxygen ($Li\text{-}O_2$) batteries have attracted interest as energy storage devices due to their high energy and power density. The first non-aqueous $Li\text{-}O_2$ battery was developed using a polyacrylonitrile (PAN) polymer based electrolyte by Abraham in 1996 [1]. These batteries when used in electric vehicles will significantly increase the driving range thus revolutionizing the automobile industry. $Li\text{-}O_2$ batteries have high theoretical specific energy density of 11,140 Wh/kg and they can achieve four times higher energy density than the current lithium ion batteries [1,2].

A typical $Li\text{-}O_2$ battery consists of a lithium anode, porous cathode which is open to oxygen and Li^+ ion conducting electrolyte separating the electrodes[3]. The electrochemical reaction taking place in $Li\text{-}O_2$ battery is as follows [4]:

$$2Li + O_2 \leftrightarrow Li_2O_2$$

Where Li_2O_2 is deposited on the surface of cathode during discharge (oxygen reduction reaction), and the reverse reaction (oxygen evolution reaction) takes place during charging to decompose Li_2O_2 on the surface of cathode. A few reports demonstrate the Li_2O formation during discharge which is difficult to reverse during charging [5,6]. Aqueous electrolytes involve formation of OH^- and then LiOH at the cathode on discharge according to equation [4]:

$$2Li^+ + O_2 + H_2O + 2e^- \leftrightarrow 2LiOH$$
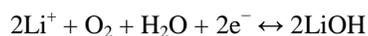
Although extensive research has been done to improve the performance of $Li\text{-}O_2$ batteries, they are still in their developmental stages and many technical challenges must be addressed before they can be commercialized. The most common problems hindering the development of $Li\text{-}O_2$ batteries are low rate capability, poor recyclability and low round-trip efficiency [3,7,8] Catalysts have shown to improve the battery capacity and the recyclability of these batteries when used in cathodes. Metal nanoparticles consist of a large surface area and are hence used in various functions and applications. Intrinsic properties of these are determined by shape, composition, size and crystallinity [9]. Nanotechnology can enhance

and provide a new lease of life for these materials. In this paper, I will discuss a few nanoparticles that are used as nanocatalysts for Li-O_2 batteries.

Several nanoparticles such as gold, rhodium, nickel, platinum, silver, palladium, ruthenium, cobalt, and other inorganic compound nanoparticles have been used as nanocatalysts for Li-O_2 batteries [8]. Debart et al. used several catalysts for lithium oxygen batteries with non-aqueous electrolyte. They used Pt, $La_{0.8}Sr_{0.2}MnO_3$, Fe_2O_3, NiO, CuO, $CoFe_2O_4$. Co_3O_4 as electrocatalysts and exhibited high discharge capacity and good cycling performance. They also studied manganese oxides as catalysts for lithium oxygen batteries. Mn_3O_4, bulk Mn_2O_3, bulk α, β, λ, γ-MnO_2, α-MnO_2 nanowires and β-MnO_2 nanowires were used as catalysts [9]. The air cathode with α-MnO_2 as the catalyst showed the highest capacity of about 3000 mA.h/g (carbon).

For my research, I investigated the battery performance of Li-O_2 batteries by coating and filling the carbon nanotubes [3]. It was observed that the Pd-filled CNTs showed a 6-fold improvement in the first discharge cycle over pristine CNTs and 35% increase when compared to Pd-coated CNTs. High discharge capacity of 11,152 mA.h/g was obtained when using Pd-filled CNTs. Encapsulation of the catalyst in CNTs assisted in improving the stability of the electrolyte by reduction in Li_2CO_3 formation.

Zhang et al. used palladium coated α-MnO_2 as a catalyst in the Li-O_2 batteries with initial discharge of 1220 mA.h/g and capacity retention rate of 47.3% after 13 cycles [10,11]. The work of Zhao et al. gives a mechanistic insight into catalytic effect between metal oxide and noble metal [12]. They designed a hybrid nanostructure using 2D Birnessite MnO_2 (δ-MnO_2) and palladium nanocrystals. The Pd/δ-MnO_2catlysed Li-O_2 batteries exhibit high capacity, low polarization and stable cycling of 133 cycles at a fixed capacity 1000 mA.h/g at a current density of 200 mA/g. The DFT calculations indicated that the presence of Pd on one side of δ-MnO_2 sheets promoted the formation of Li_2O_2 and induced the formation of stable, electronically conductive LiO_2 at the opposite side of the δ-MnO_2 sheets. MnO_2 coated on hexagonal nanoplatelets were synthesized as bifunctional catalysts by Yun Jung Li et al. for Li-O_2 batteries [13]. The hetero-structured catalyst (HSC) hybrid enhanced the electrochemical performance of the battery. They obtained 60 cycles at a fixed capacity of 1000 mA.h/g and current density of 100 mA/g.

Lu et al. developed the cathode by atomic layer deposition (ALD) of palladium nanoparticles on carbon surface with an alumina coating for passivation of carbon defect sites [14]. Pd nanoparticles on ALD surface were used as electrocatalysts to promote Li_2O_2 formation by improving electronic transport. Super P Li conductive carbon was used to support the catalyst material. 1M $LiCF_3SO_3$ in tetra-ethylene glycol dimethyl ether (TEGDME) electrolyte on glass fiber separator and lithium metal anode was used for the charge discharge cycles. After discharging to 1000 mA.h/g and charging, the charging potential was reduced to 3.2 V which is comparable to the theoretical of 3 V. The low potential could be maintained up to 10 cycles at 500 mA.h/g. The full discharge capacity obtained was 2750 mA.h/g. Degradation of lithium anode and poisoning of Pd catalyst by contaminants or passivation could be the reasons for the battery failure. Zahoor et al. synthesized α-MnO_2 nanorods and modified them with Pd nanoparticles to form Pd deposited α-MnO_2 nanostructures and used them as

electrocatalyst in the cathode for Li-O$_2$ battery [15]. Catalyst by contaminants or passivation could be the reasons for the battery failure. Zahoor et al. synthesized α-MnO$_2$ nanorods and modified them with Pd nanoparticles to form Pd deposited α-MnO$_2$ nanostructures and used them as electrocatalyst in the cathode for Li-O$_2$ battery [15]. Ketjen black cathode with the Pd deposited α-MnO$_2$ catalyst and LiTFSi salt in TEGDME as electrolyte and lithium metal anode. A discharge and charge capacity of 8526 mA.h/g at a constant current density of 0.1 mA/cm^2 was obtained with an overpotential of 1.6 V (discharge plateau at 2.7 V and charge plateau at 4.3 V).

G. Zhao et al. fabricated TiO$_2$ nanotube arrays on Ti foam and used them as substrate for Li-O$_2$ batteries [16]. RuO$_2$/TiO$_2$ cathodes exhibit good catalytic activity towards OER and exhibit a cycle performance of 130 cycles at a current of 1.77 A/g under 1000 mA.h/g.

A uniformly coated RuO$_2$ shell on the surface of core CNT was used as catalyst to prevent direct contact between CNT and Li$_2$O$_2$ thus reducing formation of Li$_2$CO$_3$ [17]. RuO$_2$-CNT catalyst increased the specific capacity to about 4350 mA.h/g at a current of 385 mA/g and exhibited a discharge and charge overpotentials of 0.21 and 0.51 V. 20 cycles were obtained at a fixed capacity of 500 mA.h/g at the current rate of 100 mA/g.

Bui et al. fabricated carbon nanofiber with platinum nanoparticles on the surface by coaxial electrospinning and observed improvement in specific capacity, rate capability, energy efficiency, cycle stability, and O$_2$ efficiency [18]. They obtained 163 cycles at the capacity limit of 1000 mA.h/g and current density of 500 mA/g.

Zhang et al. developed a novel method to synthesize NiO/CoO catalysts by pre-lithiation (PL) of pristine ternary metal oxide spinel material NiCo$_2$O$_4$ (NCO) nanowires at appropriate conditions [19]. They fabricated the PL-NCO nanoparticles on the carbon fabric. An extremely high initial capacity of ∼29 280 mA.h/g was obtained with the PL-NCO NWs/CF electrodes pre-lithiated at 0.50 V. the batteries cycled for 100 cycles at a specific capacity of >1000 mA.h/g.

Brush-like Co$_4$N nanorods were uniformly anchored on conductive electrospun carbon nanofiber (CNF) paper via hydrothermal growth of Co(OH)F nanorods followed by nitridation step by Il-Doo Kim et Al [20]. The resulting cathode exhibited cycling stability of over 177 cycles in Li-O$_2$ cells. This cycling stability was attributed to metallic Co$_4$N nanorods providing sufficient accessible reaction sites and facile electron transport pathway through the well-networked CNF. Thin oxide layer (<10 nm) formation on the surface of Co$_4$N nanorods assists in reversibility of Li$_2$O$_2$, thus reducing the overpotential gap to ∼1.23 V at 700 mA.h/g.

Sun et al. reported inverse spinel Co[Co,Fe]O$_4$/nitrogen-doped graphene (NG) composite as a catalyst for rechargeable Li-O$_2$ batteries [21]. Co[Co,Fe]O$_4$/NG catalyst in Li-O$_2$ battery exhibited an initial discharge capacity of 8236 mA.h/g and 110 cycles at a fixed capacity of 1000 mA.h/g at a current density of 100 mA/g.

We discussed a few nanocatalysts that have shown improvement in the Li-O_2 battery performance. This technology is still in developmental stages. Most of the research in the field of nano-enhanced Li-O_2 batteries in the coming years will focus on further improving the electrochemical properties of the batteries, making them safer and viable for large scale production.

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