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Graphene nanosheet supported bifunctional catalyst for high cycle life Li-air batteries

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HIGHLIGHTS

- ► Use graphene as electrochemically stable and highly conductive support matrix.
- ► $La_{0.5}Ce_{0.5}Fe_{0.5}Mn_{0.5}O_3$ catalyzes the oxygen reduction and evolution reaction.
- ► 100 cycles, average capacity of 1200 mAh g^{-1} and efficiency of 70% are achieved.

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ABSTRACT

Rechargeable lithium-air batteries offer great promise for transportation and stationary applications due to their high specific energy and energy density. Although their theoretical discharge capacity is extremely high, the practical capacity is much lower and is always cathode limited. A key for rechargeable systems is the development of an air electrode with a bifunctional catalyst on an electrochemically stable carbon matrix. The use of graphene as a catalyst matrix for the air cathode has been studied in this work. A Li-air cell using an air cathode consisting of nano-Pt on graphene nanosheets (GNS) has shown promising performance at 80% energy efficiency with an average capacity of 1200 mAh g^{-1} and more than 20 cycles without significant loss of total energy efficiency. Replacement of Pt with a bifunctional catalyst resulted in more than 100 cycles with an average capacity of 1200 mAh g^{-1} and total energy efficiency of about 70%. Electrochemical impedance spectroscopy data revealed increasing solution and charge transfer resistance during cycling, which hindered the cycle life. The increased solution resistance can be attributed to the evaporation and decomposition of electrolyte especially at high charge voltages. Further investigation on ionic liquid based electrolytes in Li-air systems is being conducted.

1. Introduction

Secondary or rechargeable batteries as energy storage devices garner more attention today than at any time in human history due to the pressure to achieve efficient and economical electrification of vehicles and storage of intermittent wind and solar energy. The specific energy of state-of-the-art rechargeable Li-ion battery packs has reached 100–120 Wh kg^{-1} for automotive propulsion applications, and further engineering optimization using currently available chemistry may yield up to about 50% higher values ($\sim$180 Wh kg^{-1}). Unfortunately, this is still insufficient to support the long term goals set by USABC in terms of full range (300 miles) electric vehicles because the required $\sim$75 kWh battery would weigh at least 400 kg and thus compromise the vehicle efficiency. Therefore further advances in specific energy are needed but are limited by low capacities of the lithium intercalation compounds used in the cathodes. One promising approach which could achieve at least 4-fold higher energy efficiency is by replacing the Li intercalation cathode with the catalytically active oxygen electrode, forming the so-called Li-air (oxygen) battery, which has the highest specific energy among all known electrochemical couples [1–9]. When only lithium is considered and oxygen is absorbed from the surrounding air environment, the battery has a specific energy of 11,972 Wh kg^{-1} in non-aqueous electrolyte systems. However, Li-air systems suffer from large discharge overpotential (η_{dis}) and charge overpotential (η_{cha}) due to slow kinetics in the oxygen reduction reaction (ORR) and in the oxygen evolution reaction (OER) [8–13]. This corresponds to low cycle life and low electrical energy efficiency, currently on the order of 60–70%. The detailed mechanisms underlying these high over voltages are currently not fully understood, but can be substantially reduced by incorporating

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appropriate catalysts. At the air-electrode (currently porous carbon cathodes), insoluble Li_2O_2 is thought to be formed via the oxygen reduction reaction (ORR). There is some evidence that, with catalysts present, Li_2O_2 will undergo the oxygen evolution reaction (OER) at sufficiently high applied recharge voltages so that the aprotic configuration could be the basis for an electrically rechargeable Li-air battery. However, the insoluble nature of Li_2O_2 in organic electrolytes, make them more prone to clog the porous structure of the air electrode. Although the theoretical discharge capacity of the Li-O_2 cell is extremely high, the practical capacity is much lower and is always cathode limited.

The first challenge is developing an efficient and low cost bifunctional catalyst which reduces both charge overpotential and discharge overpotential. Several bifunctional catalyst systems have been studied [7,13–16], such as electrolytic MnO_2 [7], α-MnO_2 nanowires, Co_3O_4, Fe_2O_3, and $CoFe_2O_4$. These results have demonstrated initial discharge capacities as high as 3000 mAh g^{-1} but declined rapidly after only a few cycles. A steady discharge potential of 2.6 V vs Li^+/Li was observed for all catalysts, however a charge voltage ranging from 4 to 4.7 V was observed, depending on the type of the catalyst used. Lu et al. demonstrated that bifunctional Pt–Au nanoparticles loaded onto Vulcan carbon were shown to enhance the ORR and OER with round trip efficiency of 77% [16]. Pt–Au/C reported in this work demonstrated a discharge capacity of 1200 mAh g^{-1} at a current density of 100 mA g^{-1} with the lowest charging voltage (3.5 V) and highest round-trip efficiency for Li-air cells. However the cycle life of this system was not well studied. In almost all cases, mesoporous carbon has been used as the support for the metal nanoparticles. Such mesoporous carbon supported electrode catalysts have shown quite moderate performance in Li-air batteries, and several major obstacles arising from the carbonaceous air cathode, such as carbon's oxidation in both charge and discharge processes, remain to be overcome if the cycling efficiency and cycle life of Li-air batteries are to be improved.

The second critical research area is the design of a high surface area and chemically stable support matrix for the bifunctional catalyst, which would prevent oxidation during charging. For the practical application of air cathodes, it is critical to choose a carbon matrix with a microstructure providing large surface area and pore volume to facilitate a Li/O_2 reaction and to hold a maximum amount of discharge products which is proportional to the battery capacity per gram of carbon. Among porous carbon materials, Super P [17], Ketjen Black [18–20] and Vulcan carbon [16] with high surface area and pore volumes have been used successfully to achieve high capacity air cathodes. However, during the charge cycle, oxygen is generated in a highly reactive form, causing highly corrosive conditions to the conductive support materials as well as to the carbonate electrolytes. Particularly, high surface area carbon materials used as a conductive support are severely attacked and oxidized (evolving CO_2) under anodic conditions [21]. This suggests that the electrochemical stability of the air cathode support material is a key challenge in the development of practical Li-air systems. As an alternative to highly porous conventional carbon, the use of single walled carbon nanotubes (SWCNT) as support materials for the air electrode has been reported [22]. Recently graphene nanosheets (GNS) as cathode support material have also been used. Bing Sun et al. demonstrated GNS as a better support with some catalytic properties compared to Vulcan XC-72 carbon [23]. An initial discharge capacity of 2332 mAh g^{-1} with an average charge potential of 3.97 V vs Li^+/Li were observed for the GNS based Li-air system. A limited cycling study of GNS (up to only five cycles) showed better performance than Vulcan XC-72 carbon. Similarly, Yoo and Zhou [24] successfully demonstrated GNS as a metal free catalyst support for Li-air batteries. Under a low current density of 0.5 mA cm^{-2}, this system showed performance comparable to a system with Pt/C up to fifty cycles. A recent paper by Peter G. Bruce et al. demonstrated the use of a nano porous gold cathode instead of a carbon based cathode, together with $LiClO_4$/dimethyl sulfoxide electrolyte in a Li-air cell to achieve 100 cycles with 95% capacity retention [9]. However, despite all these research efforts, there is still no viable low cost Li-air system with acceptable discharge capacity, round trip efficiency, and high cycle life. Therefore, research efforts need to focus on improving the capacity retention during cycling. Given the promising stability and enhanced conductivity observed in graphene, we investigated a new Li-air cathode by incorporating bifunctional catalysts into a graphene matrix. The aims of this work are twofold. Firstly, to demonstrate the use of graphene nanosheets (GNS) as an electrochemically stable, highly conductive support matrix for bifunctional catalyst in Li-air cells; and, secondly, the synthesis of novel, low cost bifunctional catalyst of the pervoskite type with the chemical composition $La_{0.5}Ce_{0.5}Fe_{0.5}Mn_{0.5}O_3$ which catalyzes the ORR and OER reactions in a working Li-air cell.

2. Experiment

2.1. Synthesis of graphene nanosheets and anchoring of nano-Pt onto GNS

The incorporation of nanoparticles of bifunctional catalyst onto GNS was performed by two methods. (1) Direct anchoring of catalyst during the synthesis of graphene from graphene oxide. (2) Use of impregnation, and co-precipitation methods to load catalyst onto as-prepared GNS.

Graphite oxide (GO) was synthesized from flake graphite (Asbury Carbons, 230U Grade, High Carbon Natural Graphite 99+) by a modified Hummers' method originally reported by Kovtyukhova et al. [25], in which pre-oxidation of graphite is followed by oxidation with Hummers' method. The pre-oxidation of the graphite power was carried out with concentrated H_2SO_4 solution in which $K_2S_2O_8$ and P_2O_5 were completely dissolved at 80 °C. The pretreated product was filtered and washed on the filter until the pH of filtrate water became neutral. The shiny, dark-gray, pre-oxidized graphite was dried in air overnight. The final oxidation of pre-oxidized graphite was performed by the reaction of pre-oxidized graphite dispersed in chilled H_2SO_4 with slow addition of $KMnO_4$ at a temperature below 20 °C. The resulting thick, dark green paste was allowed to react at 35 °C for 2 h followed by addition of 1 L of DI water to give a dark brown solution. After additional stirring for 2 h, the dark brownish solution was further diluted with distilled water after which H_2O_2 was added slowly until the color of the mixture turned into brilliant yellow. The mixture was allowed to settle overnight and the supernatant was decanted. The remaining product was washed with 10% HCl solution with stirring and the brownish solution was allowed to settle overnight. The supernatant was decanted and the remaining product was centrifuged and washed with DI water.

Pt nanoparticles on graphene nanosheets were synthesized by the ethylene glycol reduction (EG) method following reference [26]. In a typical synthesis, stoichiometric amounts of metal precursors (H_2PtCl_6 as Pt precursor) dispersed in 40 mL ethylene glycol solution and 160 mg GO dispersed in 40 mL ethylene glycol solution are mixed together in a 125 mL round-bottom flask equipped with a N_2 in/outlet. The resulting suspension is refluxed at 403 K for 3 h. The composite mixture was then sonicated for 2 h and then vacuum-filtered until the surface of the composite appeared dry. Then it is washed copiously with acetone and dried at 333 K in a vacuum oven. Finally, the catalyst-GNS composite was heat treated at 473 K under Ar–H_2 (9:1 v/v) gas atmosphere for 2 h. For comparison,