

Application of Graphene for Li-air Batteries

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Abstract: Li-air batteries have received much attention in the past several years because of their large theoretical specific energy density, stable output voltage, cost-effective, energy-efficient and pollution free, and have broad application prospects. But there are a number of challenges including poor round-trip efficiency, poor rate capability, low cycle life and poor safety characteristic to limit the practical application of the Li-air batteries. To address these issues, much research effort has been invested. In particular, graphene, with its high surface area combined with catalytic properties, is considered to be a key potential material to Li-air battery technology. Indeed, recent research into graphene has led to substantial performance improvements of Li-air batteries. In this review, we describe recent achievements in Li-air batteries that have been facilitated by the application of graphene, together with the major issues facing Li-air batteries.

Keywords: Li-air battery, Graphene, Air-electrode, Catalyst, Support

INTRODUCTION

The urgency of clean and sustainable energy has been focused on the world resurgence to explore the advanced energy storage systems and the aforementioned significant concerns conscript the energy storage devices should be of environmental benign, energy-efficient and highly durable [Datta et al., 2013]. Due to the large theoretical specific energy density, the Li-air battery is expected to be next-generation electrochemical-power source with high performance. Since Li-air batteries exploit the direct reaction between lithium ions and oxygen molecules in ambient air without any heavy transition metals or crystal frameworks, in theory, an energy density of 3500 Wh/kg is possible, which is the highest of all types of Li batteries [Bruce et al., 2012, Peng et al., 2012]. On discharge, oxygen is firstly reduced, and reacts with Li ions forming Li_2O_2 on a conductive carbon surface, which is an oxygen reduction reaction (ORR). During charging, the Li_2O_2 decomposes to evolve O_2 and produce Li ions, an oxygen evolution reaction (OER) [Oh et al., 2012]. Much advance has been achieved, however, Li-air batteries still face significant challenges in practical applications [Lu et al., 2014], including the sluggish ORR/OER kinetics related to the formation of insulating Li_2O_2 , and the accumulation of the byproducts (e.g. Li_2CO_3) due to the side reactions of Li_2O_2 (or its intermediate LiO_2) with the electrolyte or carbon. A combination of these detrimental factors results in a large overpotential, poor rate capability [Girishkumar et al., 2010], poor round-trip efficiency [Debart et al., 2008] and limited cycle life [Cheng et al., 2010] of Li-air

batteries. These problems mostly related to the materials, such as the stability of electrolyte, the air-electrode morphology and catalysts.

Graphene-based materials have received continued attention for applications in energy conversion and storage systems. Graphene contains potentially a vast active area for harvesting discharge products, which may lead to even higher capacity and enhance the kinetics in Li-air batteries. This review will summary of the recent progress in the use of graphene in Li-air batteries according to their role in the enhancement of the performance. we categorize into three major classes: graphene as a constituent of air-electrodes, graphene as a catalyst, doped graphene catalysts and graphene-supported hybrid catalysts, presented in following sections respectively.

GRAPHENE AS A CONSTITUENT OF AIR-ELECTRODES

A challenge still remains to develop high-performance and cost-effective air electrode for Li-air batteries with high capacity, enhanced rate capability and long cycle life (100 times or above) despite recent advances in this field [Liu et al., 2014]. Carbon materials is the most widely used air-electrode materials. The discharge capacity usually increases with the surface area of carbon materials. Graphene with its largest specific surface area ($2630\text{m}^2/\text{g}$), could, in principle, not only provide a large effective area for reaction sites, but also facilitate the accessibility of oxygen and Li ions [Zhang et al., 2011]. Li et al. successfully demonstrated that graphene in itself could deliver a high discharge capacity of approximately 8705 mAh/g in Li-air

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batteries [Li et al., 2011]. It was found that the discharge products grew on the graphene surface, in particular at the edges of the graphene sheets.

The advantage of the morphology of graphene could be further strengthened with the assembly of graphene. Many research groups have attempted to assemble graphene to control the size and distribution of pore in air-electrodes. Xiao et al. reported an air-electrode consisting of hierarchically porous graphene [Xiao et al., 2011]. The porous framework, comprised of numerous connected nanopores, offered diffusion paths for oxygen to access the inner space of the air-electrode. The increase in the number of reaction sites in the porous framework led to a drastically increased discharge capacity of approximately 15000 mAh/g. It demonstrates that the morphology of the carbon substrate is an important factor determining the electrochemical performance of Li-air batteries.

Graphene has also proved to be a promising constituent of air-electrode in hybrid Li-air systems composed of an organic electrolyte at the anode side and an aqueous electrolyte at the cathode side. Yoo and Zhou have examined graphene nanosheets for the use as air-electrodes in the hybrid Li-air battery [Yoo et al., 2011]. The reversible reactions of LiOH in the hybrid Li-air battery resulted in a decreased overpotential close to that of 20 wt% Pt/carbon black during discharge. Cycling up to 50 cycles was accomplished with the graphene nanosheets electrode promising the use of graphene in hybrid Li-air batteries.

According to a literature, nitrogen-doped (N-doped) graphene demonstrated 40% higher specific capacity than that of the pristine graphene in the Li-air battery [Li et al., 2012]. Moreover, it has been extensively investigated in combination with various metal oxides to create graphene/metal oxide composite materials with enhanced electrochemical activities for Li-air batteries. Park et al. synthesized a α -MnO₂ nanotubes/N-doped thermally exfoliated graphene composite which is employed as air cathode materials for Li-air battery applications [Park et al., 2013]. It is shown to demonstrate excellent ORR activity in an aprotic non-aqueous electrolyte Li-air battery resulting in 2.92V at the current density of 100 mA/g, discharge current density of 7.2 A/g at 2.2 V, and the maximum power density of 15.8 W/g based on carbon mass.

It has been reported that 3D macroporous graphene architecture can combine the superior intrinsic properties of graphene with an additional 3D porous structure, which not only maintains the high electrical conductivity and good chemical inertia of graphene, but also provides a high specific area and numerous porous channels to improve ion and electron transport [Choi et al., 2012, Wang et al., 2013]. Tu et al. proposed a unique design of a binder-free catalytic cathode for Li-air batteries. The electrode consists of a novel mushroom-like Au/NiCo₂O₄ nanohybrid on three-dimensional graphene (3D-G) grown directly

on the skeleton of Ni foam [Tu et al., 2015]. The Li-air batteries with Au/NiCo₂O₄/3D-G catalytic cathodes can deliver a discharge capacity of 1275 mAh/g. When the capacity is limited at 510 mAh/g, the Li-air battery can sustain stable cycling up to 40 times.

Liu et al. prepared binder-free 3D-G-MnO₂ air electrode by growing graphene and δ -MnO₂ directly on the skeleton of Ni foam, which inherits the interconnected 3D scaffold of Ni foam [Liu et al., 2014]. δ -MnO₂ exhibits a flower-like porous structure assembled by ultrathin nanosheets. Li-air batteries with 3D-G-MnO₂ electrode can deliver a high discharge capacity of around 3660 mAh/g at 0.083 mA/cm². The Li-air battery can keep a stable cycling of 132 times with low overpotentials at a high current density of 0.333 mA/cm². The 3D electronically conductive network also contributed to the enhanced ORR and OER kinetics.

GRAPHENE AS A CATALYST

The possibility of using graphene as a catalyst in Li-air systems has been investigated by many groups. Sun et al. first demonstrated the use of graphene as a catalyst for a Li-air battery using an alkyl carbonate electrolyte [Sun et al., 2012]. While the discharge capacity was not dramatically increased due to the similarity in the specific surface area (309 m²/g) and pore volume (0.3666 cm³/g). The decreased overpotential was attributed to the catalytic activity of carbon vacancies and defects at the graphene in the formation and decomposition of reaction products. Because defects and edges of graphene can generally exhibit higher reactivity with fast electron transfer compared to bulk graphene sheets, the formation and decomposition of reaction products can preferentially occur at those sites of graphene [Sharma et al., 2010]. However, because a carbonate-based electrolyte, which are now known to readily decompose during cycling [McCloskey et al., 2011], was used in their tests, it is not clear that the graphene acted as an OER catalyst. Nevertheless, graphene was also demonstrated to be catalytically active in aqueous based Li-air batteries by several groups [Yoo et al., 2011], where a decrease in the overpotential was observed using graphene nanosheets in hybrid electrolyte systems.

Zu et al. investigated the performance of the expandable-graphite-derived graphene sheets as the ORR catalysts in hybrid Li-air batteries. While carbon black displays a discharge voltage of 2.76 V, the expandable-graphite-derived graphene exhibits a higher discharge voltage of 2.85 V [Zu et al., 2015]. It is believed that the large amount of edges on the graphene surface act as the active sites for ORR [Yoo et al., 2011]. In addition, the graphene sheet with a two-dimensional structure allows ready access of oxygen and electrolyte from both sides, contributing to more effective mass transport and thereby higher catalytic activity.

DOPED GRAPHENE CATALYSTS

It is well known that chemical doping is an efficient strategy to improve the properties of graphene sheets and especially N doping to reduced graphene oxide (rGO) is conspicuous for the ORR [Liang et al., 2011, Wu et al., 2012]. It has been demonstrated that N doping can modify the physical and chemical properties of rGO by increasing the specific surface area of graphene [Zheng et al., 2014]. Enhanced ORR activities are achieved owing to the electron-accepting capacity of the N-dopants, creating favourable positively charged sites for side-on oxygen surface adsorption [Yao et al., 2012]. In addition, defects resulting from the N-dopants can also contribute to the anchored sites for the transition metal oxides, strengthening the interaction between the active particles and the graphene sheets [Li et al., 2013]. Moreover, the transition metal oxide nanoparticles can be better dispersed on the platform of graphene sheets with reduced particle sizes [Liang et al., 2011]. As the rational design and tailored synthetic strategy are critical factors to the catalytic performance of nanohybrids [Liang et al., 2011].

Chemically N-doped graphene has been demonstrated as a catalyst with the enhanced activity in Li-air electrode reactions [Yoo et al., 2012]. Yoo et al. investigated the catalytic properties of N-doped graphene which was obtained by the reaction of RGO and NH_3 in various conditions. The degree of nitrogen doping and the types of nitrogen sites were dependent on the process temperature. The catalytic properties of N-doped graphene are as effective as the Pt/carbon black composite that is a commonly used catalyst for ORR. Although the pristine graphene sheets also exhibited significant catalytic activity compared to acetylene black, N-doped graphene showed higher effect for ORR processes [Cheng et al., 2012].

GRAPHENE-SUPPORTED HYBRID CATALYSTS

Graphene may also be used as an effective support material for loading catalysts, such as MnO_2 , Co_3O_4 , SnO_2 , and Mn_3O_4 . Catalysts can be either physically loaded or, more often, chemically grown on the graphene. The facile formation of a triple-phase boundary in a metal oxide (MO_x)/graphene hybrid catalyst was also partly attributed to the enhanced catalytic activity. In general, the bulkier synthesis of graphene is achieved on the basis of the modified Hummers method. The resultant graphene oxide (GO) contains oxygen-containing functional groups, including carbonyl ($-\text{CO}$), hydroxylic ($-\text{COH}$), and carboxylic acid ($-\text{COOH}$) groups on the surface [Dikin et al., 2007, Cao et al., 2012]. The aforementioned negatively charged functional groups can provide reaction sites for the absorption of positively charged metal ions, such as Mn^{2+} , Co^{3+} , and Sn^{2+} . Subsequently, the metal ions and GO are reduced, either chemically or using heat treatment, yielding the composite. Meanwhile, the anchoring of

nanoparticles on reduced graphene oxide (rGO) can successfully reduce the restacking degree of rGO sheets and retain the active surface area, which is highly useful to maintain the robust stability of the prepared nanocomposite [Tian et al., 2012].

In the MO_x /graphene hybrid catalysts, it is expected that graphene enables the uniform distribution of catalyst nanoparticles, which is particularly important for Li-air batteries where the discharge products (typically Li_2O_2 , Li_2O , and Li_2CO_3) are deposited on the air-electrode in solid form [McCloskey et al., 2012]. This is in contrast to fuel-cell air-electrodes, where the liquid- or vapor-phase discharge products (H_2O) are much more mobile and do not tend to passivate the reaction sites. This distinction makes the distribution of catalysts in the electrode more important in Li-air batteries than in a conventional fuel cell. For this reason, the uniform distribution of nano-catalysts by graphene is beneficial. Also, the facile charge transport to the catalysts due to the high electrical conductivity of graphene can contribute to the cycle efficiency [Yoo et al., 2011, Xiao et al., 2011].

The graphene/cubic cobaltite oxide nanosheets ($\text{rGO}/\text{Co}_3\text{O}_4$) with a face centered cubic crystalline structure are synthesized and are exploited as effective cathode catalysts in high performance Li-air batteries [Gnana et al., 2015]. The $\text{rGO}/\text{Co}_3\text{O}_4$ composite exhibits a lower voltage, high discharge capacity of 4150 mAh/g and displays superior cyclability without any capacity losses, signifying the excellent rechargeability of the fabricated electrodes. The post mortem analysis of electrodes specify the existence of Li_2O_2 , Li_2O and Li_2CO_3 discharge products, revealing the involved electrochemical reaction of Li-air batteries. The excellent electrochemical properties of $\text{rGO}/\text{Co}_3\text{O}_4$ composite is due to the combination of rapid electrokinetics of electron transport and high electrocatalytic activity toward oxygen reduction reaction given via the synergetic effects of rGO and cubic Co_3O_4 nanosheets. These findings provide fundamental knowledge on understanding the influence of morphological and structural properties of graphene based nanostructures toward Li-air battery performances.

CONCLUSION

Recent progress in Li-air batteries was reviewed with a focus on utilizing the properties of graphene. Graphene has shown diverse applications as a constituent material for air-electrodes, a catalyst or a substrate for other catalysts. The high conducting surface area of graphene enlarged the discharge capacity. It also increased the cycle efficiency by reducing the overpotential when used as a catalyst or hybrid catalyst. Moreover, graphene was an effective substrate for hybrid catalysts, where catalysts could be uniformly grown and good adhesion between graphene and catalyst particles was possible. The catalytic activity of catalyst particles could be

enhanced by lowering the overpotential. Much advance has been achieved, but the challenges remain. It should be noted that while studies have shown improvements with graphene, most works have used carbonate-based electrolytes in their experiment. It implies that the role of graphene in Li-air batteries need to be clarified further. In addition, a full understanding of the mechanisms of discharge-charge processes and performance degradation with cycles is of equal importance for further performance improvement of Li-air batteries.

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REFERENCES

- Bruce P. G., Freunberger S. A., Hardwick, L. J., et al., 2012, "Li-O₂ and Li-S batteries with high energy storage", *Nat. Mater.* Vol.11, pp19-29.
- Cao R. G., Lee J. S., Liu M. L., Cho J., 2012, "Recent progress in non-precious catalysts for metal-air batteries", *Adv. Energy Mater.*, No.2, pp 816-829.
- Cheng F.Y., Chen J., 2012, "Lithium-air batteries: something from nothing", *Nature Chem.*, No.4, pp 962-963.
- Cheng H., Scott K., 2010, "Carbon-supported manganese oxide nanocatalysts for rechargeable lithium-air batteries", *J. Power Sources*, Vol.195, pp1370-1374.
- Choi B.G., Chang S. J., Lee Y. B., et al., 2012, "3D heterostructured architectures of Co₃O₄ nanoparticles deposited on porous graphene surfaces for high performance of lithium ion batteries", *Nanoscale*, No.4, pp5924-5930.
- Datta M.K., Epur R., Saha P., et al., 2013, "Tin and graphite based nanocomposites: potential anode for sodium ion batteries", *J. Power Sources*, Vol.197, pp316-322.
- Debart A., Paterson A.J., Bao J., et al., 2008, "Alpha-MnO₂ nanowires: a catalyst for the O₂ electrode in rechargeable lithium batteries", *Angew. Chem.Int. Ed.*, Vol. 47, pp4521-4524.
- Dikin D. A., Stankovich S., Zimney E. J., et al., 2007, "Preparation and characterization of graphene oxide paper", *Nature*, No.448, pp457-460.
- Girishkumar G., McCloskey B., Luntz A., et al., 2010, "Lithium-air battery: promise and challenges", *J. Phys. Chem. Lett.*, No.1, pp2193-2203.
- Liang, Y. Y., Li Y. G., Wang, H. L., et al., 2011, "Co₃O₄ nanocrystals on graphene as a synergistic catalyst for oxygen reduction reaction", *Nat. Mater.*, No.10, pp780-786.
- Li D, Shi D, Chen Z, et al., 2013, "Enhanced rate performance of cobalt oxide/nitrogen doped graphene composite for lithium ion batteries", *RSC Adv.*, No.3, pp5003-5008.
- Li, Y. L., Wang, J. J., Li, X. F., et al., 2012, "Nitrogen-doped graphene nanosheets as cathode materials with excellent electrocatalytic activity for high capacity lithium-oxygen batteries", *Electrochem. Commun.*, Vol.18, pp 12-15.
- Li Y., Wang J., Li X., et al., 2011, "Superior energy capacity of graphene nanosheets for a nonaqueous lithium-oxygen battery", *Chem. Commun.*, Vol.47, No.33, pp9438-9440.
- McCloskey B. D., Bethune D. S., Shelby R. M., et al., 2011, "Solvents' Critical Role in Nonaqueous Lithium-Oxygen Battery Electrochemistry", *Journal of Physical Chemistry Letters*, No.2, pp1161-1166.
- McCloskey B. D., Speidel A., Scheffler R., et al., 2012, "The twin problems of interfacial carbonate formation in non-aqueous Li-O₂ batteries", *J. Phys. Chem. Lett.*, No.3, pp997-1001.
- Oh S. H., Black R., Pomerantseva E., et al., 2012, "Synthesis of a metallic mesoporous pyrochlore as a catalyst for lithium-O₂ batteries", *Nat. Chem.*, No.4, pp1004-1010.
- Park Hey Woong, Lee Dong Un, Nazar Linda F., et al., 2013, "Oxygen Reduction Reaction Using MnO₂ nanotubes/Nitrogen-Doped exfoliated graphene hybrid catalyst for Li-air battery applications", *Journal of The Electrochemical Society*, Vol.160, No.2, ppA344-A350.
- Peng Z., Freunberger S. A., Chen, Y., et al., 2012, "A reversible and higher-rate Li-O₂ battery", *Science*, No.337, pp563-566.
- Sharma R., Baik J. H., Perera C. J., et al., 2010, "Anomalously large reactivity of single graphene layers and edges toward electron transfer chemistries", *Nano.Lett.*, Vol.10, pp398-405.
- Sun B., Wang B., Su D., et al., 2012, "Graphene nanosheets as cathode catalysts for lithium-air batteries with an enhanced electrochemical performance", *Carbon*, Vol.50, pp727-733.
- Tian L., Zhuang Q., Li J., et al., 2012, "The production of self-assembled Fe₂O₃ graphene hybrid materials by a hydrothermal process for improved Li-cycling", *Electrochim. Acta.*, No.65, pp153-158.
- Tu F. F., Xie J., Zhang S. C., et al., 2015, "Mushroom-like Au/NiCo₂O₄ nanohybrids as high performance binder-free catalytic cathodes for lithium-oxygen batteries", *J. Mater.Chem.A.*, No.3, pp5714-5721.
- Wang H., Zhang D. S., Yan T. T., et al., 2013, "Three-dimensional macroporous graphene architectures as high performance electrodes for capacitive deionization", *J. Mater.Chem.A.*, No.1, pp11778-11789.
- Wu Z. S., Yang S., Sun Y., et al., 2012, "3D Nitrogen-Doped Graphene Aerogel-Supported Fe₃O₄ Nanoparticles as Efficient Electrocatalysts for the Oxygen Reduction Reaction", *Am. Chem. Soc.*, No.134, pp9082-9085.
- Xiao J., Mei D. H., Li X. L., 2011, "Hierarchically Porous Graphene as a Lithium-Air Battery Electrode", *Nano.Lett.*, No.11, pp5071-5078.

- Yao Z., Nie H., Yang G., et al., 2012, "Catalyst-free synthesis of iodine-doped graphene via a facile thermal annealing process and its use for electrocatalytic oxygen reduction in an alkaline medium", *Chem. Commun.*, No.48, pp1027-1029.
- Yoo E., Nakamura J. and Zhou H., 2012, "N-Doped graphene nanosheets for Li-air fuel cells under acidic conditions", *Energy Environ.Sci.*, No.5, pp6928-6932.
- Yoo E. and Zhou H., 2011, "Li-Air Rechargeable Battery Based on Metal-free Graphene Nanosheet Catalysts", *ACS. Nano.*, Vol.5, No.4, pp 3020-3026.
- Zhang S.S., Read J., 2011, "Partially fluorinated solvent as a co-solvent for the non-aqueous electrolyte of Li/air battery" *J. Power Sources*, Vol.196, pp2867-2870.
- Zheng B., Wang J., Wang F. B. and Xia X. H., 2014, "Low-loading cobalt coupled with nitrogen-doped porous graphene as excellent electrocatalyst for oxygen reduction reaction", *J. Mater. Chem. A.*, No. 2, pp 9079-9084.
- Zu C. X., Li L. J., Qie L., et al., 2015, "Expandable-graphite-derived graphene for next-generation battery chemistries". *Journal of Power Sources*, No.284, pp 60-67.