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Self-standing, binder-free electrospun Co_3O_4/carbon nanofiber composites for non-aqueous Li-air batteries

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ABSTRACT

In this study, self-standing, binder-free ZIF-9 derived Co_3O_4/carbon nanofiber composites were synthesized via electrospinning and post thermal treatment for use as the cathode in a non-aqueous Li-air battery. Due to possessing a three-dimensional cross-linked web structure, Co_3O_4/carbon nanofiber composites are used directly as the cathode for Li-air batteries without the use of any binders or conductive metal foam, thus alleviating undesirable chemical reactions. We confirm that metallic cobalt (Co) in ZIF-9 is successfully oxidized to cobalt oxide (Co_3O_4) following two thermal treatment steps by analysis of XRD and XPS. The initial discharge capacity of Co_3O_4/carbon nanofiber composites exceeds 760 mAh g^{-1}, which is a much higher discharge capacity compared to pristine carbon nanofiber (72 mAh g^{-1}). Additionally, Co_3O_4/carbon nanofiber composite based cells exhibit improved cycling properties and a lower charge overpotential at various current densities. The improved electrochemical properties of the Co_3O_4/carbon nanofiber composites are attributed to the catalytic activity and stable contact with the homogeneously distributed Co_3O_4 in the carbon nanofiber structure. This work demonstrates that the synthesized Co_3O_4/carbon nanofiber composites could possibly be applied for use as next generation electrode materials for energy storage and conversion devices, particularly Li-air batteries.

1. Introduction

Toward the facilitation of rapid technological advances in the field of electrical devices, high energy storage systems are regarded as an indispensable prerequisite. Over the last few decades, researchers have developed various energy storage and energy conversion systems utilizing safe, cost-effective, and high energy density [1]. In particular, metal-air batteries, including Li-air, Zn-air, Al-air, air Mg-air [2–4], are considered to be advanced battery systems due to their light weight and high energy storage capabilities. Among the variety of metal-air battery types available, Li-air batteries have attracted enormous research attention due to their extremely high theoretical energy densities (11,140 Wh kg^{-1}) which are around 5 times higher than that of conventional Li-ion batteries [5]. In spite of these advantages, there still exist many substantial challenges to be overcome, such as low rate capabilities, poor cycle life, high overpotential, and instability of electrochemical performances [6–9]. In Li-air battery systems, the cathode is a key factor affecting both battery capacities and cyclic performances because electrochemical reactions such as Oxygen Reduction Reactions (ORR) during discharging and Oxygen Evolution Reactions (OER) during charging take place on the side of the cathode [10–16].

Reaction products, such as Li_2O_2 or Li_2O, accumulated on the cathode surface during discharging are difficult to dissolve in non-aqueous electrolytes and hinder oxygen diffusion from outside the cell. For these reasons, it is essential that the cathode of non-aqueous Li-air batteries have high electronic conductivity, large surface areas, and porous structures to facilitate electron pathways and accommodate the formation of reaction products. Another important point is that properties of the cathode are not only influenced by the cathode material but also by the method of cathode fabrication.

The most widely used cathode fabrication method for non-aqueous Li-air batteries is via casting [17–21]. Casting is a process by which conductive materials and binders are cast into conductive metal foam forming dense structures. However, employing casting in the fabrication of cathodes can cause chemical reactions leading to undesirable side reactions during the charge/discharge process. Undesirable decomposed substances such as carbonate electrolytes significantly degrade the electrochemical performance of Li-air batteries due to an acceleration of

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diffusion resistance against the electrochemically active species [22]. Furthermore, swelling, gelation, and dissolution of conventional binders such as polyvinylidene fluoride (PVDF) or polytetrafluoroethylene (PTFE) have a negative impact on battery performance [23,24]. Because of these problems, many researches have been attempted to synthesize the self-standing electrode without the need for binders or/and metal foam [25–27].

Additionally, in order to reduce overpotentials during charging-discharging, high-efficiency catalytic materials are needed, which can play a critical role in enhancing the cycling performance of Li-air batteries [16–18]. Catalysts can promote the dissociation of reaction products formed during discharging and achieve reduced charge voltages [28]. Cathode catalysts of noble metals, functional doped carbon materials, metal oxides, and metal oxide hybrids have been studied to address the poor electrochemical properties of Li-air batteries. Cobalt-based materials in particular stand out due to their excellent catalytic performance properties, including their initial capacity, capacity retention, and low charging voltages (4 V) [29].

To obtain high performance Li-air cells, the catalyst and carbon should be homogeneously mixed and electronic contact between the two materials should be stable [30–33]. Recently, carbon-metal composites for electrochemical applications have been studied, highlighting the importance of the material's catalytic properties. As a class of nanoporous materials, metal organic frameworks (MOFs) are composed of redox-active metal cations and organic ligands [34]. MOF-derived carbon-metal composites can possess exceptionally high surface areas and exhibit a uniform distribution of metals within the carbon framework. Zeolite imidazolate frameworks (ZIFs), considered to be a subclass of MOFs, were used in various applications as electrocatalysts for water oxidation, gas adsorption, and gas separation [35,36].

Herein, we introduce a cobalt-containing ZIF (ZIF-9) derived Co_3O_4/carbon nanofiber composite for non-aqueous Li-air batteries. ZIF-9 possesses a microporous crystalline structure with a composition of cobalt ions linked to benzimidazolate ligands [37]. We present a simple method for the fabrication of Co_3O_4/carbon nanofiber composite cathodes using ZIF-9 and carbon nanofiber precursors via electrospinning of a mixed solution comprising metallic cobalt and a carbonization-capable polymer (PAN). Two post-thermal treatments (carbonization and oxidation) converted ZIF-9/PAN composites to Co_3O_4/carbon nanofiber composites. Of note, we demonstrated that as-synthesized Co_3O_4/carbon nanofiber composites can be used as self-standing air cathodes without the need for binders or metal foam.

2. Experimental

2.1. Synthesis of ZIF-9/PAN nanofibers via electrospinning

We employed an electrospinning process for the synthesis of ZIF-9/PAN mixed nanofibers. To prepare precursor solutions, we dissolved 1 g of polyacrylonitrile (PAN) powder, 0.1 g of cobalt nitrate hexahydrate, and 0.08 g of benzimidazole into a 10 mL solvent of N, N-dimethylformamide (DMF). To obtain a homogeneously mixed solution, magnetic stirring was applied for 24 hours at 353 K using a hot plate under inert atmospheric conditions. The mixed solution was then drawn into a 10 mL plastic syringe with a needle (possessing an inner diameter of 0.10 mm) and ejected to form ZIF-9/PAN nanofibers by applying a 15 kV bias between the syringe needle and a rotating drum collector covered with aluminum foil. The tip to drum collector distance and solution flow rate were fixed at 15 cm and 1 mL h^{-1}, respectively. The electrospun ZIF-9/PAN fibers were collected on the aluminum foil as a fibrous mat.

2.2. Synthesis of Co_3O_4/carbon nanofiber composites

The fibrous mat was stabilized at 280 °C (at a heating rate of 5 °C min^{-1}) followed by a thermal treatment process yielding carbonized ZIF-9/carbon nanofibers at 900 °C (at a heating rate of 2 °C min^{-1}) in a horizontal quartz tube furnace under a nitrogen atmosphere maintained for 1 hour. The resultant carbonized samples were thermally oxidized under air in a muffle furnace at 280 °C for 20 minutes. Additionally, a pristine carbon nanofiber reference sample was prepared for the comparison of material and

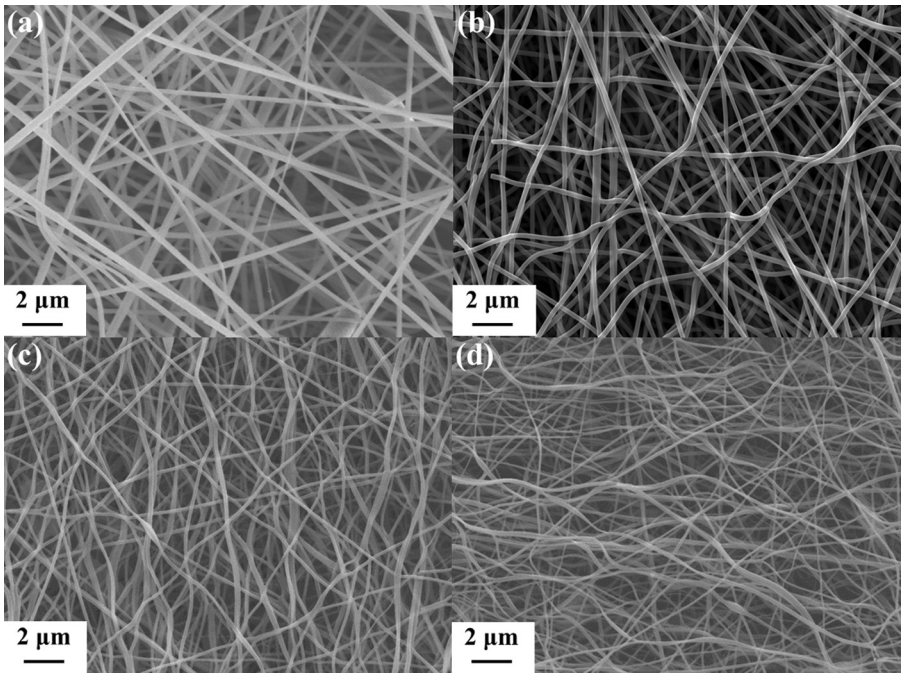

Fig. 1. FE-SEM images of the (a) electrospun PAN-based nanofibers, (b) ZIF-9/PAN nanofibers, (c) carbonized ZIF-9/carbon nanofibers, (d) after oxidation ZIF-9/carbon nanofibers.