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Full Length Article

Iron/carbon composite microfiber catalyst derived from hemoglobin blood protein for lithium-oxygen batteries

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ABSTRACT

Recycling of bio-waste sources for synthesis of functional electrode materials is an eco-friendly and sustainable approach to realize next-generation energy-storage systems. In this study, we present a fabrication method of Fe/C composite microfibers derived from electrospinning of hemoglobin blood protein, and subsequent calcination, and investigate its functionality as an oxygen electrode catalyst for Li–O_2 batteries. We elucidate the thermal decomposition behavior of raw hemoglobin protein and structural evolution after calcination at different temperatures. We successfully fabricated Fe/C composite microfibers with a uniform and flattened shape by electrospinning of a hemoglobin precursor and thermal treatment. Finally, we demonstrated that Li–O_2 cells in which the Fe/C composite microfiber catalyst was incorporated in the oxygen electrodes exhibited improved electrochemical performance compared to a pristine reference cell without the catalyst.

1. Introduction

Future energy-storage alternatives should provide a high energy capability exceeding that of current Li-ion batteries [1]. Lithium–oxygen (Li–O_2) batteries have attracted significant interest for next-generation energy storage owing to their high theoretical energy density, which is comparable to that of gasoline [2–5]. Li–O_2 batteries can be realized by satisfying certain requirements, such as a high efficiency, low environmental impact, and cost-efficiency [6]. Current Li–O_2 batteries suffer from a low reversibility, which is caused by the formation of insulating lithium–oxide products (i.e., LiO_2, Li_2O_2) for discharging and sluggish decomposition for reverse charging ($2Li^+ + O_2 + 2e^- \leftrightarrow Li_2O_2$, $E^0 = 2.96$ V versus Li/Li^+) [7–9]. Consequently, the large overpotential of over 1 V followed by slow kinetics should be addressed for the realization of Li–O_2 batteries [10,11]. Studies have been performed to overcome these issues by developing catalyst materials decorated on an oxygen electrode in a Li–O_2 cell [12–14]. In this regard, various solid catalyst materials (e.g., metal and metal oxides) have been introduced to improve the kinetic properties and reversibility of the batteries [3,15–21]. Nevertheless, further suitable catalyst alternatives should be developed for a greener and cheaper Li–O_2 battery technology.

The direct utilization of sustainable natural sources as a precursor is a preferred approach to synthesize functional catalyst materials for future energy applications [22,23]. For example, blood bio-wastes could be recycled for eco-friendly and cost-effective productions of the catalyst materials [24–28]. It is known that hemoglobin, a core component in blood, consists of four globular protein subunits bound by a non-protein prosthetic heme group [29]. The hemoglobin structure includes various organic-based atomic species (e.g., carbon, oxygen, nitrogen, iron, etc.), which can be transformed to components of a catalyst molecule, thereby providing functional properties. By controlling the synthetic conditions, various Fe-based inorganic materials with tailored morphologies can be successfully fabricated from a hemoglobin precursor [30]. The materials derived from blood protein are expected to be utilized as efficient catalysts for future Li–O_2 batteries.

In this study, we report an iron/carbon (Fe/C) composite microfiber material prepared using hemoglobin blood protein, and investigate its potential as an oxygen electrode catalyst for Li–O_2 batteries. The Fe/C microfibers can be successfully fabricated by electrospinning of a hemoglobin-containing solution and subsequent calcination under a reducing atmosphere (Fig. 1). We investigate the thermal decomposition behavior and morphologies of Fe/C derived from the hemoglobin precursor source. In addition, we observe morphological and structural features of the Fe/C microfibers. Finally, the electrochemical properties of the Fe/C microfibers are evaluated to demonstrate its catalytic activity as a potential oxygen electrode catalyst for Li–O_2 cells. The results of this study could be useful for the synthesis of various types of blood-derived materials and their applications.

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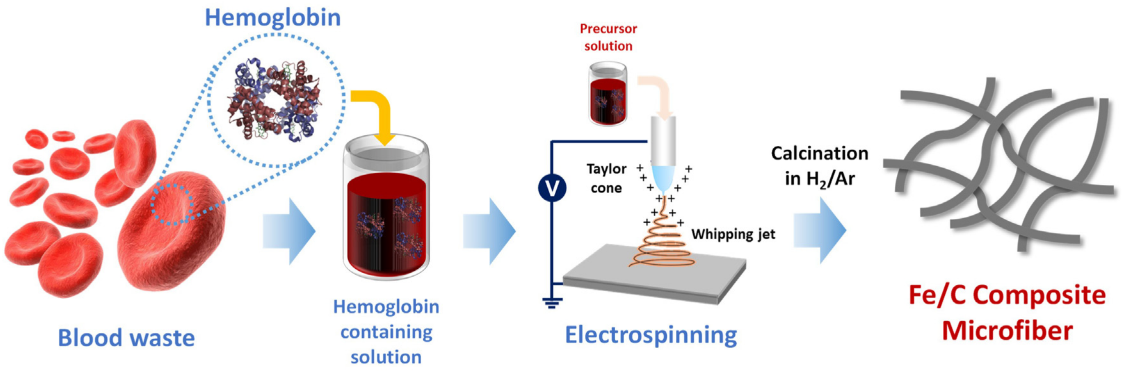

Fig. 1. Schematic illustration of the synthetic procedure of Fe/C microfibers from hemoglobin using electrospinning and calcination under a reducing atmosphere.

2. Experimental methods

2.1. Materials and chemicals

Hemoglobin from bovine blood was purchased from Sigma-Aldrich and used as received. In order to dissolve the hemoglobin for electrospinning, 2,2,2-trifluoroethanol (TFE, 99%) was used, purchased from Alfa-Aesar.

2.2. Synthesis of Fe/C powder

In the heat treatment, 0.2 g of hemoglobin was treated under an H_2/Ar (5%/95%, v/v) atmosphere at 650, 800, and 950 °C for 2 h by increasing the temperature at a rate of 10 °C min^{-1}. Each calcined sample was weighted to estimate the composition.

2.3. Synthesis of Fe/C microfiber

In order to prepare the electrospinning solution, 1.3 g of hemoglobin was dissolved in 5 mL of TFE under stirring with a magnetic bar (200 rpm) at room temperature for 12 h. The electrospinning solution was filled in a plastic syringe, which was fixed at 12 cm from a stainless foil wrapped on a cylinder collector. For the electrospinning, a voltage of 18 kV was applied using a high-voltage DC power supply and a rotation speed of 100 rpm was set with a rotating drum collector. As-spun hemoglobin microfibers were then obtained. The collected microfibers were calcined at 250 °C for 1 h under O_2 atmosphere at 10 °C/min to burn out residues in hemoglobin. A post-heat-treatment of the pre-calcined hemoglobin microfibers was then performed at 650 °C for 2 h under the H_2/Ar (5%/95%, v/v) atmosphere to carbonize and deoxidize hemoglobin.

2.4. Material characterizations

The obtained Fe–C powder and microfibers were characterized by powder X-ray diffraction (XRD, SmartLab, Rigaku) using Cu-K_α (λ = 1.54 Å) radiation. The surface morphologies of the calcined hemoglobin were observed with a scanning electron microscope (SEM, JSM-7600F, JEOL). Thermogravimetric (TGA, TG209 F3) and differential thermal (DSC, DSC404C) measurements were performed at a heating rate of 10 °C min^{-1} under an inert-gas atmosphere. Raman spectroscopy (LabRam Aramis, Horiba Jobin Yvon) was employed to analyze molecular vibrations. Surface characteristics of the microfiber sample were investigated by X-ray photoelectron spectroscopy (XPS, K-alpha, Thermo U. K.).

2.5. Electrochemical characterization

For the preparation of the oxygen electrodes, the following procedures were employed. Slurry was prepared by mixing 65 wt% of multi-walled carbon nanotubes (MWCNTs), 25 wt% of microfiber, and 10 wt% of poly(vinylidene fluoride) (PVDF) binder in an 1-methyl-2-pyrrolidinone (NMP) solvent. A flattened Ni-mesh was then covered by the slurry and dried under vacuum at 80 °C for one day. The average mass loading of electrodes was 0.045 g per 12 mm diameter Ni foam. A Li-metal foil was used as an anode; the separator was a Whatman GF/A glass microfiber. The electrolytes were produced by mixing 1 M lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in diethylene glycol dimethyl ether (DEGDME) and stirring overnight. Swagelok cells were used; the cells were assembled in a glove box filled with a high-purity argon and purged with dry O_2 out of the glove box. The electrochemical performances of the obtained fiber samples were investigated using cyclic voltammetry (CV) and full charge/discharge tests. The CV tests were performed in the voltage range of 2.0–4.5 V at different scan rates. The full charge/discharge tests were performed between 4.5 V and 2.3 V under a current density of 100 mA g^{-1}.

3. Results and discussion

In order to investigate the thermal behavior and structural feature of the hemoglobin protein after calcination, Fig. 2(a)–(c) show the morphologies of the samples obtained by burning hemoglobin at different temperatures under a reducing atmosphere. The samples prepared by calcination of hemoglobin protein exhibit planar structures with smooth surfaces. The sizes of the powder samples are approximately sub-hundred micrometer owing to agglomeration of the hemoglobin precursor during the thermal treatment. There is no significant morphological change with the increase of the calcination temperature from 650 °C to 950 °C. XRD results of the samples prepared at different calcination temperatures are shown in Fig. 2(d). The XRD peaks of all of the samples correspond to the carbon and cubic Fe phases (Joint-Committee-on-Powder-Diffraction-Standards (JCPDS) no. 26-1076 and no. 06-0696, respectively) without any impurities. Considering the various carbon sources in the protein, the partial phase in the sample could be the mixed structure of Fe and C (such as Fe_3C) structure as well as separated phases of sole C and Fe [31]. The peak intensity and crystallinity increase with the calcination temperature. There is no phase change or sub-peak related to impurities after calcination at the high temperature of 950 °C. We performed a Raman spectroscopy analysis of the sample prepared at 650 °C to further investigate structural information and carbon residues (Fig. 2(e)). We observed a weak Fe–C vibration mode related to mixture phase of Fe and C in the low wavenumber region. The weak peak feature of the Fe–C vibration mode is associated to the crystallinity. Distinct D and G peaks corresponding to the carbon phase appear at 1364 cm^{-1} and 1601 cm^{-1}, respectively [3,31]. The burned hemoglobin does not show a high crystallinity of the mixed Fe-C composite phase even after the calcination at 950 °C. It means that a large carbon amount involved in