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α-MnO_2 nanorods supported on porous graphitic carbon nitride as efficient electrocatalysts for lithium-air batteries

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HIGHLIGHTS

- g-C_3N_4 was combined with MnO_2 as cathode catalyst for Li-air batteries for the first time.
- A two-step hydrothermal method was used to prepare porous g-C_3N_4/α-MnO_2 composite.
- The porous g-C_3N_4/α-MnO_2 composite exhibits good catalytic performances in Li-air battery.

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ABSTRACT

Synthesis of α-MnO_2 nanorods grown on porous graphitic carbon nitride (g-C_3N_4) sheets via a facile hydrothermal treatment gives a porous composite exhibiting higher activity for an air cathode than the individual component of α-MnO_2 or porous g-C_3N_4 for both the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). The porous g-C_3N_4/α-MnO_2 composite also exhibits better performance in a Li-air battery than pure α-MnO_2 or XC-72 carbon catalysts, which includes superior discharge capacity, low voltage gap and high cycle stability. The α-MnO_2 nanorods catalyze the OER and the porous g-C_3N_4 sheets catalyze the ORR.

1. Introduction

With global warming, diminishing fossil-fuel supplies, and environmental pollution, it is urgent to develop storage of electric power from renewable energy sources. Rechargeable Li-air batteries have attracted considerable interest for this task due to their extremely high theoretical energy density ($\sim$11,140 W h kg^{-1} excluding O_2), which can be compared to that of a gasoline engine ($\sim$13,000 W h kg^{-1}) [1,2]. This high energy density makes them a good candidate for stationary storage of electric power if not for electric vehicles [3]. However, Li-air batteries still suffer from poor power capability, poor cyclability, and low energy efficiency [4,5]. The kinetics of the cathode oxygen-reduction reaction (ORR) and oxygen-evolution reaction (OER) are limited [6]. Many efforts have been made to develop better cathode catalysts for Li-air batteries [7–16], but these materials still suffer from low stability, low efficiency, low electronic conductivity and/or high cost, which limit their practical use in Li-air batteries.

Graphitic carbon nitride (g-C_3N_4) can be prepared from a simple precursor via a series of polycondensation reactions without any metal involvement [17–20]. Due to its special optical features, high nitrogen content, and excellent chemical stability, the material has been widely applied in photocatalysis and fuel cell [21–23]; but few investigations have been carried out on the application of g-C_3N_4 as a cathode catalyst for nonaqueous Li-air batteries [17]. Because of the planar cohesion of adjoining sheets through π-π aromatic stacking, it is often difficult to exfoliate bulk g-C_3N_4 into sheets of a few nanometers thicknesses [24]. In order to increase the surface area of bulk g-C_3N_4, T. Sano and coworkers [25] reported that the g-C_3N_4 can be treated by alkaline hydrothermal treatment to form a porous structure with a high surface area, which can offer abundant active sites. A mesoporous porous structure can also accommodate the insoluble discharge product Li_2O_2, and facilitate the transport and storage of oxygen [26], which is beneficial for g-C_3N_4 as an active electrocatalyst for nonaqueous Li-air batteries. However, the poor electroconductivity and accumulation of Li_2O_2 intermediate products in the discharge process has limited the electrocatalytic application of g-C_3N_4 [18]. Recently, several efforts

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have been made to improve the electrocatalytic activity of g-C_3N_4 by employing different modifications, such as doping, and making a composite with other materials. J Jutao [23] et al. reported a suitable loading of g-C_3N_4@cobalt oxide on graphene exhibits excellent electrocatalytic activity and a dominant four-electron oxygen reduction pathway in basic solution; the composite showed improved electrocatalytic activity for the ORR.

Among the transition metal oxides, manganese oxide (MnO_2) is a low-cost catalyst for the OER [27]. Nevertheless, its low conductivity largely limits its applications [28]. The nitrogen provides π* electrons that facilitate electron transfer from the g-C_3N_4 to adsorbed molecules [29,30]. Thus combining g-C_3N_4 with MnO_2 can theoretically improve the electrical conductivity and electrocatalytic activity.

Owing to the advantages of g-C_3N_4 and MnO_2, we present here a novel strategy to synthesize α-MnO_2 nanorods grown on porous g-C_3N_4 sheets as cathode catalysts for rechargeable Li-air batteries in nonaqueous electrolyte. The porous g-C_3N_4/α-MnO_2 composite was fabricated by a two-step hydrothermal treatment. The α-MnO_2 nanorods are uniformly distributed on the surface of the porous g-C_3N_4 sheets without affecting the porous structure. In this work, we combined g-C_3N_4 with MnO_2 as cathode catalyst for nonaqueous Li-air batteries for the first time. Moreover, we use a two-step hydrothermal method to prepare porous g-C_3N_4/α-MnO_2 composite for the first time. The composite catalyst exhibits remarkably enhanced electrocatalytic activity for a rechargeable Li-air battery.

2. Experimental section

2.1. Synthesis of bulk g-C_3N_4

The g-C_3N_4 was prepared by pyrolysis; 10 g of melamine powder was transferred into an alumina crucible with a cover and heated at 550 °C for 3 h in air with a ramp rate of 3 °C min^{-1} to obtain a yellow bulk solid of g-C_3N_4.

2.2. Synthesis of porous g-C_3N_4 sheets

In a typical procedure, 0.50 g bulk g-C_3N_4 and 40 mL NaOH solution (0.12 mol L^{-1}) were mixed into a 50 mL Teflon-lined stainless steel autoclave and heated at 150 °C for 18 h. After cooling to room temperature, the sample was centrifuged and washed three times with absolute alcohol before drying at 80 °C overnight.

2.3. Synthesis of porous g-C_3N_4/α-MnO_2 composite

0.1 g of the porous g-C_3N_4 was dissolved in 40 mL deionized water and subject to ultrasound for 30 min. After that, 0.21 g $MnSO_4 \cdot H_2O$ was added and stirred at room temperature for 30 min. Then, 0.49 g $KMnO_4$ was added and stirred for another 30 min. Finally, the mixture was transferred into a 50 mL Teflon-lined stainless steel autoclave and kept at 140 °C for 12 h. The dark brown product was collected by centrifugation, washed with deionized water and absolute alcohol, and then dried at 80 °C for 12 h. For comparison, free α-MnO_2 nanorods were also synthesized using exactly the same procedure without adding porous g-C_3N_4.

2.4. Material characterization

The crystal structure and phase purity were checked by X-ray powder diffraction (XRD) with Cu-Kα radiation from 10° to 90° (2θ). The morphologies of the samples were observed by scanning electron microscopy (SEM, SU8020, Hitachi) and transmission electron microscopy (TEM, JEM-2100 F, Hitachi). Thermogravimetric analysis (TGA) of samples was performed on a Netzsch TG/DTA thermogravimetric analyzer. X-ray photoelectron spectra (XPS, Thermo Escalab 250Xi), were recorded to confirm the surface composition. The specific surface area, pore volume, and pore size of the samples were investigated by BET and BJH models.

2.5. Electrochemical measurements

ORR and OER activities were examined with rotating disk electrode (RDE) measurements consisting of a platinum electrode as an auxiliary electrode, a saturated calomel electrode as a reference electrode, and a glassy carbon electrode (0.126 cm^2) as the working electrode; a 0.1 M KOH solution was used as the electrolyte. The catalyst powder (10 mg) and XC-72 carbon (2 mg) were dispersed in 2 mL of 5:1 (v/v) deionized water/isopropanol solvent, and 40 μL of 5 wt % Nafion solution was added into the as-prepared mixture to obtain a homogeneous ink after sonicating for 1 h; 5 μL of the ink was coated onto a polished glass carbon substrate and dried to obtain the catalyst film. The resultant electrodes were examined by linear scanning voltammetry (LSV) on a potentiostat (CHI604d) at room temperature. An ORR polarization curve was made by scanning from 0.2 to −0.7 V vs SCE at a rate of 10 mV s^{-1} in O_2-saturated 0.1 M KOH. An OER polarization curve was scanned from 0 to 1.0 V at a rate of 10 mV s^{-1} in a 0.1 M KOH solution saturated by N_2.

The electrochemical performance of Li-air batteries was studied with 2032 coin cells having holes in the cathode side. All the cells were assembled in an argon-filled glove-box with a lithium pellet as the anode, glass fiber filter paper as separator, 1 M $LiCF_3SO_3$ in TEGDME as the electrolyte, two pieces of nickel foam as the filler, and carbon paper supported catalysts as cathode electrodes. The air cathodes were formed by mixing a homogenous ink of 60 wt% XC-72 carbon, 30 wt% catalyst material and 10 wt% PVDF onto a carbon paper current collector. After coating, the carbon papers were dried in a vacuum drying oven at 80 °C for 12 h, and the resultant catalyst mass loading of the oxygen cathodes was about 0.5 mg cm^{-2}. An air electrode containing α-MnO_2 nanorods and XC-72 carbon catalysts were also prepared respectively for comparison. The as-prepared electrodes were dried in vacuum oven at 80 °C for 12 h. The discharge-charge capacities of catalysts were tested in a potential range of 2.4–4.5 V at a current density of 100 mA g^{-1}. The cycling performance of catalysts was tested by limiting the specific capacity to 1000 mA h^{-1} in a potential range of 2.0–4.8 V at a current density of 500 mA g^{-1}. The specific capacity and current density were normalized by the mass of the carbon loaded on the cathode. All the cell testing was conducted under run continuous flow of O_2 and O_2 pressure of 1 atm at room temperature.

3. Results and discussion

Fig. 1 depicts the schematic illustration of the synthetic process of porous g-C_3N_4/α-MnO_2 composite and the molecular structure of the catalytic spots of porous g-C_3N_4/α-MnO_2 composite catalyst. Fig. 2a shows the XRD patterns of g-C_3N_4 (dark cyan) and porous (g-C_3N_4 bule line). It can be seen that both samples displayed two distinct peaks. The strong diffraction peak at 2θ = 27.3° is a characteristic indicator of layered stacking, indexed as (002) peaks [25]. The lower peak at 2θ = 13.1° can be assigned to the (100) diffraction peak, which belongs to tri-s-triazine units [31]. The (002) peak is broadened after the alkaline hydrothermal treatment (the inset in Fig. 2a), which reflects that the alkaline hydrothermal treatment can reduce the grain size of g-C_3N_4 [32]. The (100) peak is not observed after the alkaline hydrothermal treatment. These results illustrate that the intrinsic crystal structure of g-C_3N_4 has been maintained.

Fig. 2a (red and black line) displays the XRD patterns of α-MnO_2 and the porous g-C_3N_4/α-MnO_2 hybrid. The typical reflection peaks at 2θ of 12.7°, 17.8°, 28.7°, 37.4°, 41.8°, 49.7°, 56.2°, 60.1°, 65.4°, and 69.3° can be indexed to the tetragonal α-MnO_2 phase [13]. The peak at 2θ of 25.7° is attributed to porous g-C_3N_4. In this way, the co-existence of the above two components in the composite has been confirmed.

Fig. 3a and b displays the SEM images of bulk g-C_3N_4, and porous g-