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Carbon-sphere/Co_3O_4 nanocomposite catalysts for effective air electrode in Li/air batteries

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HIGHLIGHTS

- A carbon-sphere/Co_3O_4 nanocomposite is introduced as a catalyst for the air electrode.
- Co_3O_4 nanoparticles were homogeneously dispersed on the surface of carbon spheres.
- This will increase the carbon/catalyst contact area acting as the catalytic active site.
- The electrode containing carbon-sphere/Co_3O_4 nanocomposite showed high capacity.
- It also presented low over-potential, and relatively stable reversibility.

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ABSTRACT

As a new approach to the development of advanced Li/air batteries, a carbon-sphere/Co_3O_4 nanocomposite is introduced as a catalyst for the air electrode. Co_3O_4 nanoparticles are dispersed homogeneously on the surface of carbon spheres in an attempt to increase the carbon/catalyst contact area acting as the catalytic active site during the electrochemical reaction. A high discharge capacity, relatively stable reversibility, and low overpotential are observed in electrochemical tests of an electrode containing this carbon-sphere/Co_3O_4 nanocomposite. This indicates that the carbon-sphere/Co_3O_4 composite is a promising catalyst for the air electrode of Li/air batteries.

1. Introduction

Li/air batteries are currently the most promising new rechargeable batteries because they have much higher energy densities than other energy-storage systems such as lithium-ion batteries [1–7]. The high energy density of the Li/air cell is attributed to the fact that the cathode active material (oxygen) is not stored in the battery, but is instead supplied from the environment. Specifically, oxygen is reduced catalytically on an "air electrode" surface, and reacts with the lithium cations supplied by the anode to form Li_2O_2 (or Li_2O) on the air electrode during the discharge process [8–10]. Theoretically, if oxygen was supplied without limit, the Li/air battery could be discharged until the entire lithium anode had reacted with oxygen. However, in practical applications using organic electrolytes, the energy density of a Li/air cell falls short of the theoretical value. Previous studies have suggested that insoluble reaction products such as lithium peroxide (Li_2O_2) may block the catalytic active site, preventing O_2 intake and Li^+ delivery to the active reaction site and terminating the discharge process [11–13]. Therefore, the practically available capacity of the Li/air battery is highly dependent on the properties of the air electrode. Moreover, the air electrode significantly affects the rechargeability and overpotential of the Li/air cell [8–13].

In general, an air electrode is composed of a catalyst, carbon, and a binder. Although some carbon itself has a catalytic property, this is not typically sufficient to dissociate the reaction products. So it has been known that the oxide catalyst such as Co_3O_4 needs for superior catalytic activity of the air electrode. However, the oxide catalysts should be contacted with carbon to compensate for their poor electronic conductivity. Considering the reaction model of the air electrode [12], most active sites may be catalyst/carbon contact areas in the air electrode. Accordingly, it is expected that the use of an air electrode with a wide catalyst/carbon contact area will enhance its catalytic activity. To date, most air electrodes have been

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prepared by mechanical mixing of carbon with a catalyst [8–10]. However, such mechanical mixing might not disperse a nanosized catalyst perfectly on the carbon surface. Thus, it has been difficult to obtain a sufficient catalyst/carbon contact area.

In the present study, carbon spheres were introduced as a new carbon frame for combination with an oxide catalyst. Our study was motivated by the notion that a carbon sphere with homogeneous surface energy (due to its spherical shape) will facilitate the uniform dispersion and coating of a nanocatalyst on the carbon surface. Thus, the carbon-sphere/catalyst nanocomposite could offer a wide carbon/catalyst contact area, which may act as the catalytic active site. Moreover, the carbon sphere would compensate for the insufficient electronic conductivity of the oxide catalyst. In this work, a carbon-sphere/catalyst composite was fabricated, and its electrochemical properties as the air electrode in a Li/air cell were characterized. Co_3O_4 was adopted as the oxide catalyst because of its attractive catalytic activity in various application fields [14–16]. The air electrode containing Co_3O_4 has showed high capacity and relatively stable cyclic performance. The carbon-sphere/Co_3O_4 nanocomposites are expected to show enhanced catalytic activities as electrode materials for Li/air cells owing to their wide catalytic active areas and improved electronic conductivities.

2. Experimental

Carbon-sphere templates were prepared from D-glucose precursors using a modified hydrothermal synthesis process [17,18]. Typically, glucose (3 g) was diluted in deionized (DI) water and mixed by magnetic stirring. The mixture was then sonicated continuously for 10 min until a clear solution was formed. This solution was subsequently transferred to a Teflon-lined stainless-steel autoclave and thermally treated in an electric oven at 180 °C for 14 h. Next, black products were recovered by centrifugation and washed with water and alcohol. Finally, the as-synthesized samples were dried overnight in a vacuum oven at 90 °C. To check the degree of defect of prepared carbon sphere, Raman spectrum was obtained using a Raman spectrometer (Horiba Jobin Yvon, LabRam Aramis).

The carbon-sphere/Co_3O_4 nanocomposite was prepared by impregnating carbon spheres with a cobalt nitrate solution, through the dispersion of 2.5 g of carbon spheres in 100 mL of a 0.05 M cobalt nitrate solution under sonication. This mixture was sonicated at room temperature, stirred magnetically for 24 h, and then washed once with water. Subsequently, the powder was dried overnight in an oven at 80 °C, after which it was calcined at 400 °C under a N_2 atmosphere. The fabrication process for the composite is shown in Fig. 1. The X-ray diffraction (XRD) patterns of the compound were obtained using a Rigaku X-ray diffractometer with monochromatized Cu-Kα radiation ($\lambda = 1.5406$ Å). The microstructure of the compound was observed using field-emission scanning electron microscopy (SEM, JEOL-JSM 6500F) and transmission electron microscopy (TEM, JEOL-JEM 2100F). The carbon-sphere/Co_3O_4 ratio was analyzed using thermogravimetry (TG, STA S-1500) at a scanning rate of 10 °C min^{-1} from 25 to 800 °C in an air atmosphere. The electrochemical performance of an air electrode containing the carbon-sphere/Co_3O_4 nanocomposite as a catalyst was examined using a modified Swagelok cell consisting of an air electrode, a metallic lithium anode, a glass filter separator (Whatman), and an electrolyte composed of 1 M LiTFSi in tetraethylene glycol dimethyl ether (TEGDME). The air electrode contained carbon (Ketjenblack (KB) pore volume $\approx$ 3.21 cm^3 g^{-1}), the catalyst (carbon-sphere/Co_3O_4 nanocomposite, pore volume $\approx$ 0.038 cm^3 g^{-1}), and a binder (polyvinylidene difluoride, PVDF). The weight ratio of catalyst/carbon/binder was adjusted to 72:18:10. Because the weight ratio of carbon spheres to Co_3O_4 was 71:29 in the composite, the Co_3O_4 (oxide catalyst) ratio of the electrode containing the composite was $\approx$21 wt%.

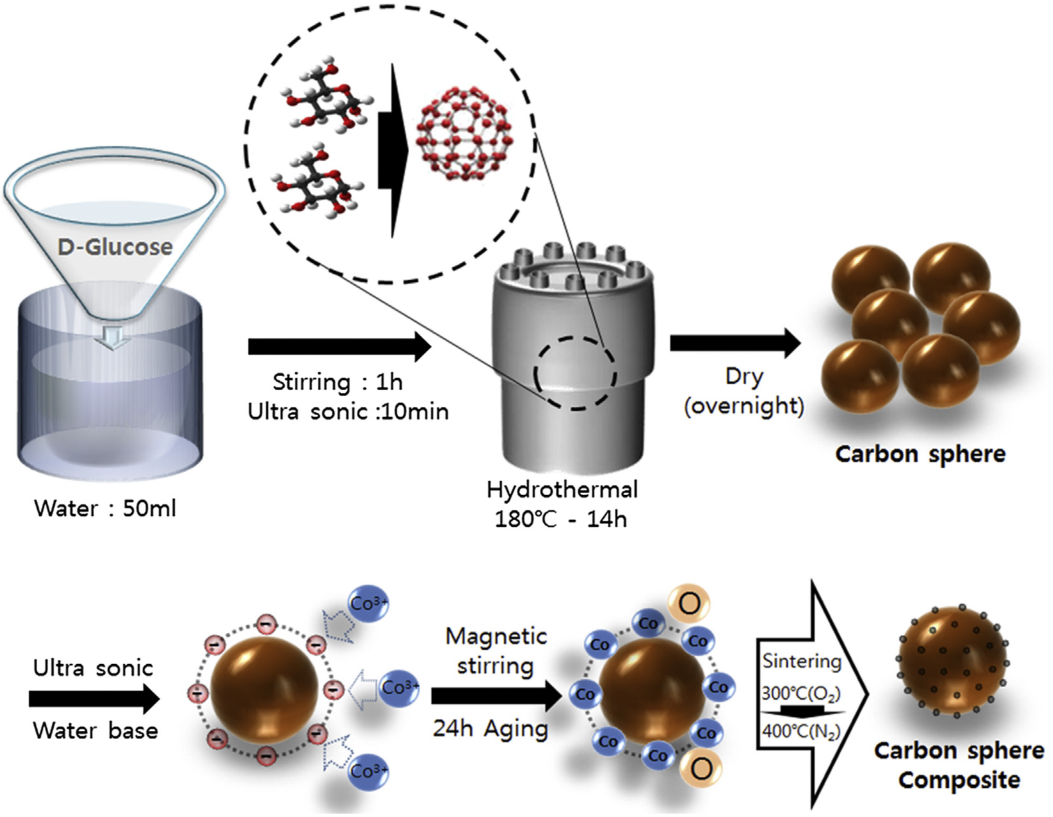

Fig. 1. Schematic of the synthetic procedure used to obtain carbon-sphere/Co_3O_4 nanocomposite.