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Rational design of protective In$_2$O$_3$ layer-coated carbon nanopaper membrane: Toward stable cathode for long-cycle Li-O$_2$ batteries

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ABSTRACT

To date, lithium-oxygen batteries (LOBs) using porous carbon materials as the air cathode have been widely studied. However, a fundamental issue of carbon electrode still remains; the carbon surface is unstable and is highly reactive in contact with Li$_2$O$_2$, resulting in the formation of irreversible byproducts (*e.g.*, Li$_2$CO$_3$). To address this issue, we investigated the use of surface protection layers for improving the cycling stability of porous carbon-based LOB cathode. We employed atomic layer deposition (ALD) for conformal coating of two types of overlayers (In$_2$O$_3$ and TiN), *i.e.*, oxide and nitride thin film, on an electrospun carbon nanopaper (CNp) membrane. The LOB cell with In$_2$O$_3$-coated CNp exhibited much enhanced cycling performance (over 140 cycles) compared with pristine CNp and TiN-coated CNp as control samples (less than 60 cycles for both cases). To further improve cell efficiency by reducing overpotentials, the surface of In$_2$O$_3$-coated CNp electrode was functionalized by catalytic RuO$_x$ nanoparticles, which enables stable and complete discharging and recharging reactions below 4.2 V for an extended period of 165 cycles. Interestingly, after each discharge, nanosheet-like Li$_2$O$_2$ growth was observed on In$_2$O$_3$-coated CNps, which is advantageous for enhanced cycle life. This work demonstrates that use of a free-standing, high surface area carbon membrane, that is conformally encapsulated by a highly conductive and stable oxide protection layer, is essential for enhanced Li-O$_2$ cell performance by preventing direct contact between underneath carbon and electrolyte.

1. Introduction

Lithium-oxygen (Li-O$_2$) batteries have recently attracted a great deal of attention as next energy storage technologies due to their high energy density (3505 W h kg^{-1}) [1,2]. However, present Li-O$_2$ batteries suffer from a poor performance such as a low capacity, poor round-trip efficiency and short-cycle life; such problems are mainly determined by cathode materials and structural design for producing a porous O$_2$-breathing air cathode [3]. In the cathode, pores can be easily clogged by Li$_2$O$_2$ that is deposited on the cathode, deactivating interfacial areas for oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) (2Li$^+$ + 2e$^-$ + O$_2$ $\rightleftharpoons$ Li$_2$O$_2$). Moreover, a common organic binder unavoidably undergoes chemical decomposition. Specifically, the commonly used polyvinylidene fluoride (PVDF) binder is decomposed by nucleophilic attack of the superoxide radicals [4,5]. This has stimulated numerous research on porous, binder-free cathode [6,7].

Carbon-based cathode materials have been designed to build free-standing air electrodes in many different forms such as carbon nanotubes (CNTs), 3D graphene foam, and carbon cloth composed of carbon fibers (CFs) due to their high electronical conductivity, light weight, and low cost [8–10]. Without binder, more stable reaction on carbon-based cathodes can be expected through stable maintenance of many desirable pores and catalytic sites as well as facile passage for electrons and oxygen gas. However, a major drawback of the carbon-based cathode remains unresolved; it was reported that carbon in contact with Li$_2$O$_2$ is easily oxidized, and especially, defects on carbon tend to trigger electrolyte decomposition, resulting in irreversible formation of lithium carboxylates (HCO$_2$Li and CH$_3$CO$_2$Li) and especially Li$_2$CO$_3$ [11,12]. Eventually, such byproducts are irreversibly converted to CO$_2$ and H$_2$ at a high charge potential (> 4.0 V *versus* Li/Li$^+$) [13].

Thus far, extensive efforts have been devoted to addressing the above critical problems of carbon-based electrodes. Kang et al. demonstrated that an ionic solvate of dimethoxyethane (DME) and lithium nitrate (LiNO$_3$) can partially eliminate CO$_2$ evolution from CNT

electrode by deactivating defect sites [14]. Lee et al. employed surface modification method to cover entire carbon surfaces [15]. They coated ultrathin insulating polyimide layer on CNT, which was able to operate for a long-time with suppressed parasitic reactions. Although these studies have demonstrated significant progresses, it is still unclear whether the electrode design including electrolyte additives and insulating coatings assures long-term stability of carbon electrode and guarantees fast electron transfer between poorly conductive binder and Li_2O_2 during cycling or not; therefore, straightforward approach to fabricate porous, free-standing carbon cathode surrounded by stable and conductive protection layer is highly demanded.

In this work, we report a porous and free-standing carbon nanopaper (CNp) encapsulated by In_2O_3 thin film (CNp@In_2O_3) and catalytic RuO_x nanoparticles (NPs) (RuO_x-CNp@In_2O_3), as a highly efficient Li-O_2 cathode. In_2O_3 has a high electronic conductivity ranging from 10^{-4} Ω cm to 6.3×10^{-5} Ω cm [16]. An amorphous In_2O_3 coating layer that is unreactive to superoxide and peroxide species ($O_2^{-\cdot}$, LiO_2, O_2^{2-}, LiO_2^- and Li_2O_2) and has a high electronic conductivity can be conformally formed on CNp by using atomic layer deposition (ALD) [17], which prevents direct contact between CNp and electrolyte. In_2O_3 surface layers prepared by this process can be very stable because deleterious side reactions are minimized. The importance of using conductive oxide protection layer on elecrospun CNps performance was also highlighted *via* direct comparison with ALD grown TiN-coated CNp and pristine CNp. With highly effective RuO_x catalyst for ORR and OER, the Li-O_2 batteries using RuO_x-CNp@In_2O_3 exhibited outstanding battery performance along with low overpotentials during discharge and charge. Furthermore, through ex-situ analyses, we demonstrated the mechanism by which Li_2O_2 grows and is removed on surfaces of overlayers and how passivated CNp has a high stability upon generation and decomposition of Li_2O_2 in Li-O_2 batteries.

2. Methods

2.1. Synthesis of free-standing carbon nanopaper (CNp)

Firstly, polyacrilonitrile (PAN) Np was prepared *via* the electrospinning with solution including 1 g of PAN dissolved in 6 g of *N,N*-dimethylformamide (DMF). Plastic syringe, 23-G stainless needle and metallic collector were used for the electrospinning. The blended solution was electrospun with conventional electrospinning equipment (NanoNC, ESR200RD). The feeding rate of the solution was 20 µl min^{-1}. A high voltage of 20 kV was applied between the needle and the collector. After the electrospinning, the electrospun PAN Np was thermally treated in box furnace at 250 °C for 1 h in air atmosphere. Then, for carbonization, the stabilized Np was heated up to 1000 °C with heating rate of 10 °C min^{-1} and maintained for 2 h in tube furnace surrounded by flowing Ar atmosphere. After cooling down, the CNp was finally achieved.

2.2. Atomic layer deposition of In_2O_3 on carbon nanopaper (CNp@In_2O_3)

The ALD of In_2O_3 onto the CNp was conducted using an ALD system (Lucida 100, NCD Co. Ltd.). Triethyl-indium (TEIn) was used as the indium precursor and ozone was utilized as reactant. N_2 was employed as the carrier and purging gas, and its flow rate (50 sccm) was adjusted by a mass flow controller. Based on the ALD growth rate per cycle (GPC), we controlled the thickness of the In_2O_3 deposited on the CNp. The CNp, as substrate for the ALD, were maintained at 200 °C, and the GPC of the TEIn precursor was saturated at about 0.63 Å/cycle. In this work, two different samples were obtained, which are the CNp coated by In_2O_3 overlayer with size of 25 nm and 50 nm after 397 cycles and 794 cycles of the growth rate, respectively.

2.3. Atomic layer deposition of TiN on carbon nanopaper (CNp@TiN)

To coat TiN on CNp, tetrakis-dimethyl-amino-titanium (TDMAT, 99.999% purity, DNF Co. Ltd) was used as ALD source. One cycle of ALD was composed of 1) exposure of TDMAT, 2) Ar purge, 3) N_2 plasma and 4) Ar re-purge. 25 nm-thick TiN coating layer was homogeneously covered on CNp after 200 cycles of ALD.

2.4. Coating of RuO_x nanoparticles on CNp@In_2O_3

RuO_x NPs were randomly coated on the surfaces of the CNp@In_2O_3-50 according to previous report [18]. The CNp@In_2O_3-50 was dipped into 0.1 M $RuCl_3$ solution followed by sonication for 10 min. Then, by dropping 0.3 M $NaHCO_3$ aqueous solution into the above solution, we could make the solution including RuO_x NPs growing on CNp@In_2O_3-50 at pH 7.0. After another stirring for 15 h, the precipitate was rinsed several times with distilled water. Finally, it was thermally treated in air atmosphere at 150 °C for 1 h.

2.5. Electrochemical measurements using Li-O_2 cells equipped with air cathode

For evaluation of the Li-O_2 cells with various air cathodes (CNp, CNp@In_2O_3, RuO_x-CNp@In_2O_3, CNp@TiN), Swagelok-type cells were assembled according to our previous work [19]. Prior to the Li-O_2 cell operation, free-standing CNp-based air cathodes without additional conducting agents and binders were prepared by synthetic method explained above. The weight of air cathode was calculated based on mass of whole papers; while the weight of the CNFs was 0.5 mg cm^{-2}, those of the CNFs with In_2O_3 and/or RuO_2 NPs coating layers were 0.6–0.7 mg cm^{-2}. All of the Li-O_2 cells were assembled in glovebox filled with pure Ar (water content was less than 0.5 ppm). Li metal was used as counter electrode, and glass fiber (Whatman GF/F) and carbon paper with 5 wt% of PTFE (CNL Energy, GDL 10BC) were utilized as separator and gas diffusion layer, respectively. The Li-O_2 battery electrolyte was 85 µl of 1 M LiTFSi in TEGDME without any additives. Electrochemical performances were investigated by carrying out galvanostatic charge-discharge experiments at a current density of 0.2 mA cm^{-2} with various restricted capacities between voltage range of 4.8 and 2.0 *versus* Li/Li$^+$ with a battery testing system (Multicycling Battery Test System) under 1 atm O_2 gas flowing.

2.6. Material characterization

The morphological elemental characterizations of all the air cathodes before and after reactions were investigated by a field emission scanning electron microscopy (FE-SEM, Nova 230, FEI), high resolution transmission electron microscope and energy-dispersive X-ray spectroscopy with scanning transmission electron microscope (tecnai F30 S-Twin, FEI for HR-TEM, EDS and STEM). X-ray diffraction (XRD, D/MAX-RB (12 kW) X-ray diffractometer, RIGAKU Co., Japan) and a Sigma-Probe X-ray photoelectron spectroscopy (XPS, Thermo VG Scientific, UK) were used for characterization of different kinds of products after discharge and charge. Raman spectroscopy was carried out using a LabRAM HR UV/Vis/NIR PL (Horiba Jobin Yvon). In order to confirm various products from parasitic side reactions, Fourier transform infrared (FT-IR, IFS66v/s & Hyperion 3000, Bruker) spectroscopy was conducted.

3. Results and discussion

Fig. 1 shows the synthetic strategy for fabricating thin In_2O_3 film-coated CNp functionalized by RuO_x catalysts. Firstly, to avoid parasitic side reactions stemming from common binder, free-standing and porous CNp, which was scaled up to approximately 15 cm × 20 cm size, was synthesized using electrospinning followed by subsequent two step heat