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Conformal Coating of Heterogeneous CoO/Co Nanocomposites on Carbon Nanotubes as Efficient Bifunctional Electrocatalyst for Li-Air Batteries

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ABSTRACT

The effective design of noble-metal-free electrocatalysts is critical for improving the stability and cyclability of Li-air batteries. In this report, CoO/Co nanoparticles are conformally decorated on the surface of CNTs by a facile chemical bath deposition followed by thermal annealing. In a simulated air environment, Li-air battery with the CNTs@CoO/Co electrocatalyst exhibits a dramatic reduction of charge voltage overpotentials (0.39 V) and good cycling stability (110 cycles) as compared with that made with bare CNTs. The superior electrochemical performances are ascribed to the prior and strong absorption of LiO_2 on the surface of CoO/Co, which can alleviate the formation of side-products, then leading to a decreased overpotential. The synergistic effect between CoO/Co and CNTs can also provide more catalytic sites for the ORR/OER, promoting the formation/decomposition reversibility of Li_2O_2. These results confirm that the CNTs@CoO/Co electrode can be a promising electrocatalyst for Li-air batteries.

1. Introduction

Recently, the rechargeable Li-air batteries have attracted great interests as good candidates for next generation electrical energy storage, as they possess a much higher energy density in comparison with Li-ion batteries and other rechargeable battery systems [1–4]. Li-air batteries are based on the electrochemical reaction $2Li + O_2 \leftrightarrow Li_2O_2$ with a thermodynamic potential of 2.96 V, which involves both the oxygen reduction reactions (ORRs) for the formation of Li_2O_2 during the discharging process and the oxygen evolution reactions (OERs) for the decomposition of Li_2O_2 during the charging process [5–7]. The extremely high theoretical energy density (3504 Wh kg^{-1}) and environment friendly reaction systems of Li-air batteries are expected to meet the stringent requirements for electric-vehicles [8–11]. However, key limitations of Li-air batteries, such as low energy efficiency, poor rate capability and poor cycling, must be resolved for practical use [12–16]. Poor electrochemical performance of the Li-air batteries is mainly ascribed to the excessive accumulation of the discharge products Li_2O_2 that are not reversibly decomposed during the charging process. These products block the pathway of electrolyte and oxygen and lead to serious polarization, which account for energy efficiency of less than 80% in Li-air batteries [2,17–19]. To address these issues, it is essential to explore air electrode with highly efficient electrocatalysts which catalyze oxygen reduction reactions (ORRs) and oxygen evolution reactions (OERs) in nonaqueous media.

To date, carbon materials like CNFs, CNTs and graphene have been widely applied as electrode materials for Li-oxygen battery, owing to their high conductivity, low cost, and ease of fabrication [12,20–25]. Carbon cathode can provide void space to accommodate the generated discharge products Li_2O_2. However, in practice,

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side products from synergistic effects between carbon and the electrolyte/lithium peroxide cause the structural degradation of carbon cathode. This structural degradation of carbon cathode inevitably increases overpotential during the charging and discharging processes, and restricts the cycle life of Li-oxygen battery [26–29]. Precious metal/transition metal oxide-doped carbon materials have been recognized as one of the most promising electrocatalysts to reduce the overpotential and improve the reversibility of Li-oxygen batteries. A series of carbon nanotube encapsulated noble metal particles (Pd, Pt, Ru, and Au) hybrids have been found effective in providing uniform coverage of Li_2O_2 on CNTs surfaces and suppressing localized distribution of Li_2O_2 aggregation [30–34]. For instance, the oxygen electrode with core-shell-structured CNT@RuO_2 composite can effectively avoid the direct contact between the CNT and Li_2O_2, reduce polarization of the cathode and improve rate and cycling performance of the Li-oxygen battery [31]. Unfortunately, such highly stable noble metal catalysts are very expensive and scarce. Therefore, designing noble metal free oxides and carbon materials hybrids would be a better option for commercial Li-air batteries [35,36]. Co-based oxides have been reported to be mixed with carbon materials as cathode catalysts for Li-air batteries [37–41]. In these composites, Co-based oxides show favorable adsorption configuration of Li_2O_2 during the electrochemical process, improving the cycling life of Li-air batteries. However, few reports have been studied to prepare CNTs@CoO/Co as electrocatalysts for Li-air batteries.

In this study, CoO/Co supported on CNTs hybrid electrocatalysts are obtained through a simple two-step process of chemical bath deposition and calcination reactions. The as-prepared CoO/Co shell is able to modify the surface electron density of CNTs. The unique structure also provides sufficient space for Li_2O_2 deposition and O_2 diffusion. As expected, Li-air battery with CNTs@CoO/Co composites exhibits good rate capability, and stable cyclability in a simulated air environment (80% Ar: 20% O_2).

2. Experimental

2.1. Synthesis of CNTs@CoO/Co nanocomposites

CNT (purchased from Shenzhen Company) was first treated with nitric acid (6 M, 50 mL) at 70 °C for 3 h. The CNT (40 mg) was then dispersed in a 100 mL solution containing 5 mmol of $Co(NO_3)_2$ and 100 mmol of urea by ultrasonication for 30 min. The mixture was kept at 80 °C for 2 h in an oil bath with strongly stirring. After another 12 h for aging, the sediments were washed several times with distilled water and ethanol, then dried at 60 °C for 12 h. Finally, the as-obtained sample was calcinated at 400 °C for 2 h with a slow heating rate of 1 °C min^{-1} to convert the precursors to CNTs@CoO/Co composites.

2.2. Characterization

The crystal structure of catalyst was characterized using a Siemens X-ray diffractometer (XRD) with a Cu Kα radiation (λ = 1.5405 Å). X-ray photoelectron spectroscopy (XPS) measurement was collected using a VG ESCA-LAB 220i-XL UHV surface analysis system with a monochromatic Al Kα X-ray source (1486.6 eV). The catalyst morphology was observed in a JOEL JSM-820 scanning electron microscope (SEM) (Hitachi, Japan). Transmission electron microscopy (TEM) and high-resolution electron microscopy (HR-TEM) were obtained using a JEOL JEM-2100F. Raman scattering was performed on Renishaw 2000 Raman microscope with 633 nm argon ion laser. Brunauer-Emmett-Teller (BET) surface area was performed on a Quantachrome Nova 1200e Surface Area Analyzer.

2.3. Electrochemical measurements

The electrochemical performances of the samples were measured by using a coin-cell type Li-air battery ((type CR2032), which contains a lithium metal anode, electrolyte (1 M LiTFSI in tetraethylene glycol dimethyl ether (TEGDME)), a glass fiber separator, and a porous electrode. The catalyst slurry in the cathode was prepared by mixing an aqueous solution of CNTs@CoO/Co composites with KB carbon and PVDF at a weight ration of CNTs@CoO/Co: KB: PVDF = 60: 30: 10. The slurry was continually mixed for one day in a sealed vial. The obtained ink was casted on a carbon paper (Toray Teflon carbon paper, TGP-H-060) by successive brush-painting, followed by drying at 80 °C for 24 h in vacuum to remove the solvent (NMP). The typical loading of air electrode was about ~0.4-0.5 mg cm^{-2}. The CNTs electrode materials were obtained in a similar way using the substitution of CNTs@CoO/Co by CNTs. All the cells were assembled in the Ar-filled glove box with a H_2O and O_2 content below 0.5 ppm. In order to prevent the Li foil from reacting with water and other gasses other than oxygen, the batteries were tested at room temperature in a container filled with dry 80% Ar and 20% O_2 at 1 atm on an Arbin BT-2000 battery tester. The capacities and current densities were calculated on the mass of catalyst in the air electrode. The batteries with CNTs@CoO/Co and CNTs as cathode materials were tested at different current densities. The cells were cycled with a discharging voltage limit of 2 V and a charging voltage limit of 4.7 V at room temperature. Electrochemical impedance spectroscopy (EIS) measurements were performed at OCV through a Zahner IM6 electrochemical workstation with an AC amplitude of 5 mV.

3. Results and Discussion

The crystallinity and phase information of the CNTs@CoO/Co was studied by X-ray diffraction (Fig. 1a). Two types of Co characteristic peaks are observed, which corresponds to the standard CoO phase (JCPDS: 75-0418) and Co phase (JCPDS: 15-0806). The mixture of amorphous hump and distinguished peaks with relatively low intensities suggest the low crystallinity of the as-prepared CNTs@CoO/Co. The diffraction peak at 26.10° is related to the (002) plane of the carbon in the CNT@CoO/Co [31,42,43]. To further identify the elemental composition and the surface electronic states of the as-synthesized CNTs@CoO/Co, X-ray photoelectron spectroscopy analysis was conducted. The C 1 s spectrum is fitted according to the following carbon bonding environment: 284.5 eV, 285.2 eV (C-C), 286.1 eV (C-O-R (R = C, H)), and 288.3 eV (C = O) (Fig. 1b). The peaks located at 530.1 eV, 531.1 eV and 532.3 eV is associated with the binding energy of O-Co, O-H, and O-C, respectively, which results from cobalt oxide on or near the surface of CNTs (Fig. 1c). For Co 2p spectrum (Fig. 1d), it is observed that two main peaks of Co in CNTs@CoO-Co located at 781.7 eV and 797.7 eV correspond to $Co_{2p3/2}$ and $Co_{2p1/2}$, respectively [44–46]. After deconvolution, the peaks at 778.1 eV and 793.2 eV are assigned to Co^0, indicating the partial reduction of CoO by carbon at a high temperature.

The surface defects of CNTs examined by the relative intensity ratio of D band (1349 cm^{-1}) and G band (1581 cm^{-1}) were presented by the Raman Spectra (Fig. 2a). The CNTs@CoO/Co sample displays a larger intensity ratio of D/G (1.11) as compared with that of pristine CNTs (0.99) and the oxidized CNTs without CoO/Co particles (0.96) (Fig. S1). This result suggests the as-obtained CNTs@CoO/Co sample has more defects due to the coating of CoO/Co on the surface of carbon nanotubes. On the basis of the N_2-sorption measurement (Fig. 2b), the specific surface areas of CNTs@CoO/Co and CNTs samples are 160 and 50 m^2 g^{-1}, respectively. The lower surface area of the CNTs@CoO/Co sample is ascribed to the presence of CoO/Co on the surface of CNTs.