



# Highly ordered and ultra-long carbon nanotube arrays as air cathodes for high-energy-efficiency Li-oxygen batteries



Ruimin Yu <sup>a,b</sup>, Wugang Fan <sup>a</sup>, Xiangxin Guo <sup>a,\*</sup>, Shaoming Dong <sup>a,b,\*\*</sup>

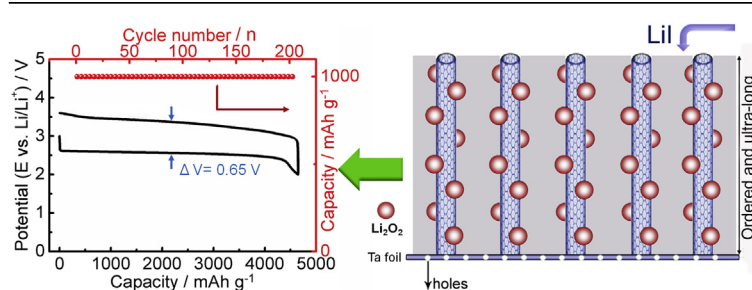
<sup>a</sup> State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China

<sup>b</sup> School of Physical Science and Technology, ShanghaiTech University, Shanghai 200031, PR China

## HIGHLIGHTS

- Highly ordered and ultra-long CNTs on permeable Ta foil were synthesized.
- The energy efficiency of Li–O<sub>2</sub> cells reached 82% with LiI catalyst.
- Their cycling performance superseded other two less ordered CNTs.
- Ordered structure benefited the transportation of Li<sup>+</sup> ions, gas and electrons.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Carbonaceous air cathodes with rational architecture are vital for the nonaqueous Li–O<sub>2</sub> batteries to achieve large energy density, high energy efficiency and long cycle life. In this work, we report the cathodes made of highly ordered and vertically aligned carbon nanotubes grown on permeable Ta foil substrates (VACNTs-Ta) via thermal chemical vapour deposition. The VACNTs-Ta, composed of uniform carbon nanotubes with approximately 240 μm in superficial height, has the super large surface area. Meanwhile, the oriented carbon nanotubes provide extremely outstanding passageways for Li ions and oxygen species. Electrochemistry tests of VACNTs-Ta air cathodes show enhancement in discharge capacity and cycle life compared to those made from short-range oriented and disordered carbon nanotubes. By further combining with the LiI redox mediator that is dissolved in the tetraethylene dimethyl glycol based electrolytes, the batteries exhibit more than 200 cycles at the current density of 200 mA g<sup>-1</sup> with a cut-off discharge capacity of 1000 mAh g<sup>-1</sup>, and their energy efficiencies increase from 50% to 82%. The results here demonstrate the importance of cathode construction for high-energy-efficiency and long-life Li–O<sub>2</sub> batteries.

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## 1. Introduction

With the growing demand for high-energy-density storage systems, nonaqueous Li–O<sub>2</sub>/air batteries have received much attention due to their ultra-high theoretical specific energy density (~3500 Wh kg<sup>-1</sup>, based on the reaction of 2Li<sup>+</sup> + O<sub>2</sub> + 2e<sup>-</sup> ↔ Li<sub>2</sub>O<sub>2</sub>) [1–5]. Different from conventional Li-ion batteries, Li–O<sub>2</sub> batteries

\* Corresponding author.

\*\* Corresponding author. State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 200050, PR China.

E-mail addresses: [XXGuo@mail.sic.ac.cn](mailto:XXGuo@mail.sic.ac.cn) (X. Guo), [smdong@mail.sic.ac.cn](mailto:smdong@mail.sic.ac.cn) (S. Dong).

could harvest active materials (i.e. O<sub>2</sub>) from atmosphere and convert chemical energy into electrical one. The reversible discharge and charge cycles are accomplished through formation and decomposition of lithium peroxide (Li<sub>2</sub>O<sub>2</sub>) in porous cathodes [5–7]. However, Li–O<sub>2</sub> batteries are still facing great challenges, such as low energy efficiency, poor cycle performance and low rate capability [8–10]. For high-performance Li–O<sub>2</sub> batteries, the architectures of cathodes should not only facilitate the transportation of ions, electrons and gas species but also provide sufficient space to accommodate the solid products formed upon discharging [11,12].

To date, various carbon electrodes such as porous carbon [13,14], carbon fibres [15,16], graphene [11,17,18] and carbon nanotube (CNT) composites [9,19,20] have been selected as the cathodes, owing to their highly electronic conductivity, tunable porosity, light weight and low cost. Among them, nanostructured CNTs have been regarded as one of the most efficient oxygen cathodes for reversible Li–O<sub>2</sub> batteries, as they could be modified easily by surface chemistry to enhance catalytic activities and prolong cycle durabilities [9,19–21] and could readily visualize the morphological and compositional changes of reactions products during cycling operation [22–24]. Previous research also implies that the improvement of CNTs in orientation order and surface area could greatly improve the battery performance [25].

In addition, introducing catalysts or “promoters” into the cathodes of Li–O<sub>2</sub> batteries has been reported as a mean to reduce the battery polarization [19,26,27]. Compared with conventional solid catalysts (precious metals, transitional oxides etc.), soluble redox mediator (RM), such as LiI [28], tetrathiafulvalene (TTF) [29], tetramethylpiperdinyloxy (TEMPO) [30] and 10-methyl-10H-phenothiazine (MPT) [10], show more efficient effect on decrease of the overpotential. This is attributed to the effective contact of dissolved RM with the insulating Li<sub>2</sub>O<sub>2</sub> deposits during charge [28]. In this sense, the highly ordered and ultra-long CNTs with the large surface area should be advantageous to improve the reaction between the RM dissolved in the liquid and the Li<sub>2</sub>O<sub>2</sub> solids deposited on the CNTs surface, benefiting the decrease of charge overpotential.

In this work, highly vertically aligned CNTs (VACNTs) with ultra-length on permeable tantalum foils were fabricated by a thermal chemical vapour deposition (TCVD) method [31,32]. The tip-growth process for the VACNTs arrays is proposed. As the air cathodes for non-aqueous secondary Li–O<sub>2</sub> batteries, the VACNTs-Ta deliver much larger specific capacities and show better rate capability than the cathodes made from entangled CNT powder and commercial VACNTs. The electrochemical reaction during the discharge-charge procedure was studied by cyclic voltammetry (CV) measurement and reaction products analysis. In combination with soluble LiI catalyst, their cycle life is further extended to more than 200 times at 200 mA g<sup>−1</sup> with a cut-off discharge capacity of 1000 mAh g<sup>−1</sup>. The charge overpotential is reduced to be as low as 0.65 V, corresponding to an energy efficiency of 82%.

## 2. Experimental

### 2.1. Preparation of VACNTs-Ta

The Ta foils (1 × 1 cm<sup>2</sup>, 25 μm thick) were punched with square matrix holes of 2 μm in diameter and 5 mm in space by a laser marker (YLP-F20T). They were ultrasonically cleaned with acetone and deionized water for several times, and dried in vacuum oven. Then two layers, a 20-nm-thick Al<sub>2</sub>O<sub>3</sub> buffer layer and a 2-nm-thick Fe catalyst layer, were deposited by electron beam evaporation on Ta foils. The VACNTs grown on Ta foils were carried out by TCVD method. The TCVD system and detailed preparation process were

given in Fig. S1. Typically, the Fe catalyst was first reduced by H<sub>2</sub> at 700 °C for 10 min, then ethane (C<sub>2</sub>H<sub>2</sub>) was introduced at 700 °C for 1 h. The as-prepared VACNTs were used as the cathodes after drying in vacuum oven at 80 °C for 12 h.

### 2.2. Electrochemical measurement

VACNTs-Ta were assembled into Swagelok-type cells with 0.5-mm-thick lithium foils as anodes and glass fibres (Whatman) and polymer films (Asahi Kasei) as separators. The average area and weight of VACNTs for each cathode were 1 cm<sup>2</sup> and 0.4 mg, respectively. The used electrolyte was 1M bis (trifluoromethane) sulfonamide lithium salt (LiTFSI, Aldrich) in tetraethylene glycol dimethyl (TEGDME, Aldrich) unless otherwise specified. 0.05 M LiI (Aladdin) was added into the above 1 M TEGDME electrolyte as the soluble catalyst.

The Li–O<sub>2</sub> cells were assembled in an Ar-filled glovebox (Braun) with O<sub>2</sub> and H<sub>2</sub>O levels below 0.1 ppm. Then, the cells were transferred into stainless steel air-tight containers with flowing high-purity O<sub>2</sub>. The discharge-charge behaviours were studied by Arbin BT2000 battery tester system after 4-h rest. The electrochemical impedance spectroscopy (EIS) measurement was performed with Autolab instrument in frequency range of 0.1–10<sup>5</sup> Hz under an ac voltage amplitude of 20 mV. Under each condition, several Li–O<sub>2</sub> cells were tested to ensure the reproducibility. The VACNTs-Ta cathodes disassembled from cells were rinsed with certain amount of anhydrous acetonitrile (CH<sub>3</sub>CN) in the Ar-filled glovebox and dried on a filter paper before characterization.

Commercial VACNTs on stainless steel mesh substrate (VACNTs-SS) were purchased from Microphase Co., Ltd and used as the cathode after drying in vacuum oven for overnight. CNTs in powder form (CNT-P, Shenzhen Nanoport Co., Ltd) with 20–40 μm in length and 15 nm in outer diameter were used as the disordered CNT for reference. They were mixed with polytetrafluoroethylene (PTFE, 60 wt %, Aldrich) solution (in weight ratio 90:10) and constructed into cathodes on stainless steel meshes. The loading of each CNT-P cathode was approximately 0.4 mg cm<sup>−2</sup>. The reported specific capacities were all calculated based on the mass of carbon nanotubes.

Morphologies of the samples were obtained by using a field-emission scanning electron microscope (FE-SEM, FEI Magellan 400) with energy dispersion spectrometer (EDS) accessory. Microstructures of the samples were observed by a high-resolution transmission electron microscope (HR-TEM, JEOL JSM-6700F) operating at 200 kV. XRD patterns were collected using a Bruker D8 Discover diffractometer. Molecular structures of CNTs were recorded on a Raman spectroscopy (Thermo Nicolet) with a laser excitation wavelength of 532 nm. Nitrogen adsorption-desorption measurement was conducted using a Tristar 3000. Chemical compositions of the VACNT surfaces were characterized by X-ray photoelectron spectrometer (XPS, ESCALAB-250) with an Al anode source. And the sample was pre-sputtered using 2 kV argon ions at the pressure of 3 × 10<sup>−9</sup> Pa for 3 s. CV measurements were carried out on Autolab utilizing homemade three-electrode electrochemical cells. Each cell was composed of a dual reference electrode, a platinum mesh counter electrode, and a glassy carbon working electrode in diameter of 3 mm. The dual reference electrode was made referring to Ref. [33]. It is composed by an Ag/Ag<sup>+</sup> electrode and a platinum wire. The former electrode consists of a silver wire dipped in an electrolyte of 0.1 M AgCF<sub>3</sub>SO<sub>3</sub>/TEGDME and separated with a Vycor frit. The potential of the dual reference electrode was −3.6 V vs Li/Li<sup>+</sup> with respect to 0.1 M LiClO<sub>4</sub> in TEGDME. More details on XRD characterization device and CV measurement can be found in our previous work [21,23].

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