



One-dimensional porous $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{2.91}$ nanotubes as a highly efficient electrocatalyst for rechargeable lithium-oxygen batteries



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ABSTRACT

The electrochemical performance of one-dimensional porous $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{2.91}$ nanotubes as a cathode catalyst for rechargeable nonaqueous lithium-oxygen (Li-O_2) batteries is reported here for the first time. In this study, one-dimensional porous $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{2.91}$ nanotubes were prepared by a simple and efficient electrospinning technique. These materials displayed an initial discharge capacity of 7205 mAh g^{-1} with a plateau at around 2.66 V at a current density of 100 mA g^{-1} . It was found that the $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_{2.91}$ nanotubes promoted both oxygen reduction and oxygen evolution reactions in alkaline media and a nonaqueous electrolyte, thereby improving the energy and coulombic efficiency of the Li-O_2 batteries. The cyclability was maintained for 85 cycles without any sharp decay under a limited discharge depth of 1000 mAh g^{-1} , suggesting that such a bifunctional electrocatalyst is a promising candidate for the oxygen electrode in Li-O_2 batteries.

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1. Introduction

Rechargeable Li-O_2 batteries are a focus of current research interest due to their very high theoretical energy density of $11,000 \text{ Wh kg}^{-1}$, which is close to that of conventional gas-powered engines [1–3]. This high specific capacity is mostly due to the fact that Li-O_2 batteries use ambient oxygen rather than storing it internally, furthermore lithium metal is used at the anode instead of a composite material. The basic chemical reactions in a non-aqueous electrolyte Li-O_2 batteries involve the formation of Li_2O_2 during the discharging process (oxygen reduction reaction or ORR) and the decomposition of Li_2O_2 during the charging process (oxygen evolution reaction or OER). However, the practical energy density of Li-O_2 batteries is much less than the theoretical prediction and the rates of these reactions are too sluggish to meet the requirements for practical applications [4,5]. In addition to the energy density, Li-O_2 batteries also suffer from other key

limitations including extremely low power density, low round-trip efficiency, instability of the electrolyte, and especially poor cyclability [6,7]. These deficiencies must be resolved in order for the Li-O_2 batteries to be considered for extensive commercial applications. There have been many efforts to improve the cyclability of Li-O_2 batteries with most of this research focusing on the development of highly active bifunctional catalysts which can effectively enhance the ORR and OER kinetics [8,9].

The adoption of highly efficient cathode catalysts with architectures that are able to accommodate or catalyze discharge products, such as Li_2O_2 , Li_2O , etc., have been reported to affect the power density, energy efficiency, and cycle life somewhat [5]. An ideal cathode requires a highly conductive porous structure to facilitate both electron and oxygen transport. Recently one-dimensional nanostructured materials, such as nanotubes, nanowires and nanofibers, have attracted much attention for use as cathode catalyst materials for oxygen electrodes [10–17]. These nanowires or nanofibers can form porous networks with randomly interconnected pore structures, which can facilitate oxygen transport for the respective electrode. To obtain the one-dimensional nanostructured catalysts materials applicable to lithium oxygen battery, various methods, such as chemical vapour

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deposition [10], co-precipitation [11], hydrothermal [12–14], in situ redox [15] and electrospinning [16,17] methods have been employed to date.

Among the methods used for the fabrication of nanostructured materials, electrospinning is a simple and efficient technique for synthesizing one-dimensional nanostructured materials with high specific surface areas and porous structures. In addition, perovskites, having a general formula of ABO_3 , are interesting oxygen electrode catalysts because of their high oxide ion mobility. By partially substituting a cation A' for A, or a cation B' for B, with a different valence, ionic defects or changes in the valence states of the catalytically active metal B can be induced in the perovskite thereby influencing its catalytic activity and conductivity [18–20]. Among the $LaMO_3$ ($M = Ni, Co, Fe, Mn, \text{ and } Cr$) materials which have been used for modified rotating ring-disk electrodes, $LaCoO_3$ showed the largest ORR current density and most positive onset potential. This material therefore offers a clear direction for further study of transition-metal cation substitution [21]. It is therefore unsurprising that $La_{0.5}Sr_{0.5}CoO_{3-\delta}$ has been considered as a catalyst for high performance lithium oxygen battery batteries. Mai et al. [22] demonstrated that hierarchical mesoporous perovskite $La_{0.5}Sr_{0.5}CoO_{2.91}$ nanowires were high-performance catalysts for the ORR with a low peak-up potential and a high limiting diffusion current. While $Li-O_2$ batteries based on such nanowires exhibited a high capacity, their cycling stability has not been reported. Herein, we demonstrate the cycling stability of a Li -oxygen battery, containing one-dimensional porous $La_{0.5}Sr_{0.5}CoO_{2.91}$ nanotubes, with interconnected particulates, produced by an electrospinning technique combined with a post-annealing process for first time. When used as cathodes in $Li-O_2$ batteries with non-aqueous electrolytes, the $La_{0.5}Sr_{0.5}CoO_{2.91}$ nanotubes provided effective pathways for the reacting species to reach the reaction sites, thereby enhancing the specific capacity and the cycle stability.

2. Experimental

2.1. Synthesis of materials

All the chemical reagents were analytical grade and used without further purification. The porous nanotubular $La_{0.5}Sr_{0.5}CoO_{2.91}$ was prepared by the electrospinning technique. Typically, $La(NO_3)_3 \cdot 6H_2O$, $Sr(NO_3)_2$ and $Co(CH_3COO)_2 \cdot 4H_2O$ with a $La/Sr/Co$ molar ratio of 1:1:2 together with polyvinylpyrrolidone (PVP) were dissolved in N,N -Dimethylformamide (DMF) under magnetic stirring to form a homogeneous viscous pink solution. The resulting solution was loaded into a plastic syringe with a 20-gauge stainless steel nozzle. The electrospun fibers were collected on a grounded plate covered with an aluminium foil. The $La_{0.5}Sr_{0.5}CoO_{2.91}$ nanofibers were fabricated with an applied electric voltage of 15 kV~20 kV between the collector and the needle tip. Finally, the electrospun nanofibers were calcined at 800 °C for 2 h (heating rate of 1 °C min⁻¹) in order to obtain the final porous product.

2.2. Characterization of samples

The phase structures of the $La_{0.5}Sr_{0.5}CoO_{2.91}$ materials were determined by X-ray diffraction (Rigaku Ultima IV, Cu K α radiation, 40 kV, 40 mA). The measurements were conducted over the scanning angle range of 10–80° at a scan rate of 0.02° min⁻¹. The morphology and microstructure were examined by SEM (SEM, QUANTA FEG 250) and HRTEM (JEOL-2010, Tokyo, Japan). The energy dispersive X-ray spectroscopy (EDX) attached to the SEM instrument was used to confirm the composition of the samples. The BET surface area was determined from N_2 sorption isotherms by using an Autosorb-iQ2-MP-C system.

2.3. Electrochemical measurements

The electrochemical performance of $Li-O_2$ cells was measured using using 2025-type coin cell. The oxygen cathodes were prepared by coating a homogenous ink composed of a mixture of 30 wt% $La_{0.5}Sr_{0.5}CoO_{2.91}$ nanotubes catalyst, 60 wt% Super P (SP), 10 wt% polyvinylidene fluoride (PVDF) or 90 wt% Super P, 10 wt% PVDF onto a carbon paper (TGP-H-060 carbon paper, Torray) current collector. The prepared electrode was dried for 12 h at 100 °C under vacuum to remove the residual solvent. R2025 coin type $Li-O_2$ cells were assembled in an argon filled glove box (MBRAUN, $H_2O < 0.5$ ppm, $O_2 < 0.5$ ppm). The cell consisted of an oxygen cathode, a glass filter (Whatman grade GF/D) separator, non-carbonate electrolyte containing 1 M $LiCF_3SO_3$ in tetraethylene glycol dimethyl ether (TEGDME) and a metallic lithium foil anode. The discharge/charge cycling was controlled by a LAND-CT2001A tester under an oxygen atmosphere. The cycling charge/discharge tests were performed with the cut-off capacity of 1000 mAh g⁻¹ at a current density of 200 mA g⁻¹. The capacity was calculated based on the mass of the carbon loaded on the cathode.

Linear scanning voltammogram of the catalysts were conducted using an RDE, and were performed using a CHI660 electrochemical station in a typical three-electrode cell. 1 mg of $La_{0.5}Sr_{0.5}CoO_{2.91}$ or 1 mg of Super P was dispersed in a mixture of 985 μ L of ethanol and 15 μ L of Nafion to prepare a homogeneous ink, a 10 μ L drop of this ink was put onto a glassy-carbon disk electrode and used as the working electrode. A platinum wire and an Ag/AgCl electrode were used as the counter electrode and reference electrode, respectively. 0.1 M aqueous KOH was used as the electrolyte. The linear sweep voltammetry was obtained at a scan rate of 10 mV s⁻¹ in the potential range -0.8 to +0.2 V (ORR) or 0.4–1.0 V (OER).

3. Results and discussion

The X-ray diffraction (XRD) pattern of $La_{0.5}Sr_{0.5}CoO_{2.91}$ nanotubes after the sintering process is shown in Fig. 1. It reveals that all the diffraction peaks could be indexed to well-crystallized $La_{0.5}Sr_{0.5}CoO_{2.91}$ nanotubes (JCPDS No. 48-0122) with a perovskite-type oxide structure. No other diffraction peaks were found, which indicated that the products were composed of pure $La_{0.5}Sr_{0.5}CoO_{2.91}$.

The surface morphology features of electrospun $La_{0.5}Sr_{0.5}CoO_{2.91}$ fibers and nanotubes was studied using SEM with an acceleration voltage of 20 kV and are presented in Figs. 2a and b. From the low-magnification SEM image of as-spun $La_{0.5}Sr_{0.5}CoO_{2.91}$ fibers (Fig. 2a), we can clearly observe a highly interconnected network of smooth nanofibers with diameters in

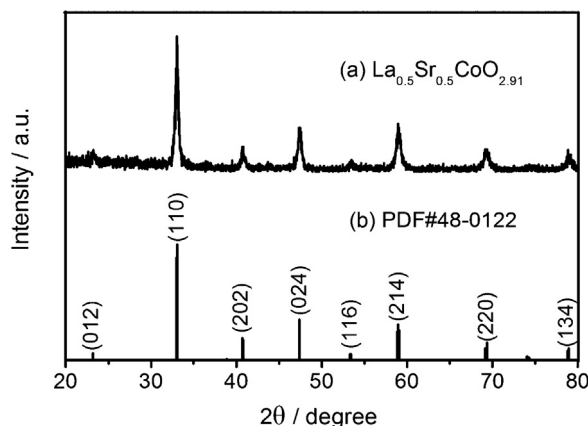


Fig. 1. (a) XRD pattern of the $La_{0.5}Sr_{0.5}CoO_{2.91}$ nanotubes. (b) Standard XRD pattern of $La_{0.5}Sr_{0.5}CoO_{2.91}$.

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