



A non-carbon cathode electrode for lithium–oxygen batteries



Z.H. Wei, P. Tan, L. An, T.S. Zhao*

Department of Mechanical and Aerospace Engineering, The Hong Kong University of Science and Technology, Clear Water Bay, Kowloon, Hong Kong SAR, China

HIGHLIGHTS

- A non-carbon cathode for lithium–oxygen batteries is proposed.
- The new electrode is prepared by depositing MnO₂ on stainless steel felts.
- This electrode renders a high capacity and good cycle stability.

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ABSTRACT

Carbon materials have been widely used to form cathodes for non-aqueous lithium–oxygen batteries. A critical problem with the use of carbon in this type of battery, however, is corrosion. To address this issue, we propose and fabricate a non-carbon cathode electrode consisting of MnO₂-deposited stainless steel (SS) felts. Amorphous MnO₂ layer are electrodeposited on the surfaces of SS fibers at an anodic current in a manganese acetate solution. The use of the MnO₂–SS electrode in a non-aqueous lithium–oxygen battery delivers a specific capacity of 1780 mA h g_{MnO₂}⁻¹. Furthermore, the discharge/charge cycle test with a fixed capacity of 500 mA h g_{MnO₂}⁻¹ shows that this electrode can discharge/charge for more than 10 cycles without degradation. It is, therefore, expected that this novel non-carbon and stable cathode is a promising electrode for high-performance lithium–oxygen batteries.

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1. Introduction

Due to its high capacity and high energy density, the lithium–oxygen (Li–O₂) battery has attracted much attention [1,2]. Based on the electrolytes used, the lithium–oxygen battery can be divided into four categories: non-aqueous, aqueous, solid state, and mixed non-aqueous/aqueous [3]. For non-aqueous lithium–oxygen battery, Li₂O₂ is the main discharge product with a stable electrolyte, and the corresponding oxygen reduction/evolution reactions (ORR/OER) during discharge/charge can be expressed as:



In a typical non-aqueous lithium–oxygen battery system, efforts have been devoted to the synthesis of cathodic catalysts and supporting materials. Carbon-based materials, including active carbon [4–7], carbon nanotube [8–10] and graphene-based carbon [11–15], have been widely used as catalysts, current collectors, and catalyst supporters, respectively. It has been shown, however, that both the discharge product (Li₂O₂) and the highly oxidizing

environment can lead to the decomposition of carbon-based materials [16]. By using ¹³C isotope labeling in the cathode electrode, ¹³CO₂ was found to exist in the final products during the charge process, proving the decomposition of carbon-based materials. X-ray absorption near edge structure also showed the formation of Li₂CO₃-like species at the interface between vertically aligned carbon nanotubes and Li₂O₂ [17]. Muhammed et al. [18] also concluded that the carbon electrode should be operated at the condition of charging Li₂O₂ below 3.5 V. The accumulation of the irreversible decomposition products (Li₂CO₃-like species) on carbon-based materials will increase the charge transfer resistance and the charge potential, subsequently leading to capacity fading.

For the above-mentioned reason, non-carbon materials have been proposed to form the cathode for the lithium–oxygen battery. For example, a free-standing-type Co₃O₄–Ni foam cathode was prepared by coating Co₃O₄ nanorods on the surface of Ni foam without additional carbon supporters [19]. The developed cathode showed a much higher catalytic activity than the same material with carbon supporters did. On the other hand, however, it has been reported that caution needs to be taken with the use of Ni in the battery operating a potential higher than 3.5 V [20]. Recently, a porous gold electrode was also used as the cathode in a lithium–oxygen battery with dimethyl sulfoxide (DMSO) as the electrolyte

* Corresponding author. Tel.: +852 2358 8647.

E-mail address: metzhao@ust.hk (T.S. Zhao).

[21], with a lower charge potential than that of the carbon-based cathode. The issue with the use of gold as electrodes is, however, the high price, limiting its practical applications. Thus, it is still challenging to find a suitable cathode supporter that is resistant to corrosion and also cost effective.

Manganese oxide has been proven to exhibit high catalytic activity for lithium–oxygen batteries, but its use has been limited to carbon-based electrodes [22–24]. In this work, we propose a new type of non-carbon cathode consisting of stainless steel (SS) felt as the supporter and deposited MnO_2 layer as the catalyst. The following features of the new cathode are expected: (i) as this non-carbon cathode can avoid irreversible Li_2CO_3 -like species produced from electrode decomposition, a lower charge potential could be achieved; (ii) owing to its good stability, the SS substrate is more suitable for cathodic supporters [25,26]; and (iii) MnO_2 is a promising catalyst because of its high abundance, low cost, environmental friendliness and excellent catalytic performance for both ORR and OER [27,28]. In addition, the deposition method to form the electrode proposed in this work is very straightforward.

2. Experimental

2.1. Electrodeposition of manganese oxide catalyst

Analytical grade chemicals manganese acetate ($\text{C}_4\text{H}_6\text{MnO}_4 \cdot 4\text{H}_2\text{O}$, Tianjin Damao Chemical reagent factory, China) and anhydrous sodium sulfate (Na_2SO_4 , VWR International, Belgium) were used as received. Two pieces of SS felt with the thickness of 300 μm were cleaned with a 0.5 M- H_2SO_4 solution, rinsed with distilled water (DI) and acetone, and then air-dried. 6.0 cm^2 of SS felt was then immersed in the solution containing 0.5 M Na_2SO_4 and $\text{C}_4\text{H}_6\text{MnO}_4$ to be used as the cathode. The other piece of clean SS felt was used as the anode. The MnO_2 was obtained by electrodeposition on one side of the immersed SS felt in the galvanostatic regime at a cathode current density of 1.0 mA cm^{-2} with stirring. After that, the deposited film was rinsed with DI and then dried at 60 $^\circ\text{C}$ for 12 h. The mass of MnO_2 film was controlled to be 1.0 mg cm^{-2} by adjusting the electrodeposition time and confirmed by weighing the substrates before and after deposition.

2.2. Characterizations

The surface morphologies of the SS felt and the MnO_2 -SS electrode were determined by scanning electron microscopy (SEM, JEOL-6300). A scanning electron microscopy with energy dispersive X-ray spectroscopy (SEM-EDX) mapping was operated at 20 kV to analyze the surface element distribution. X-ray photoelectron spectroscopy (XPS) was carried out using a Physical Electronics PHI-5600 spectrometer to investigate the valence of Mn. The crystal structures of the MnO_2 electrode were analyzed with a Philips high resolution X-ray diffraction system (model PW1825) using a $\text{Cu K}\alpha$ source operating at 40 keV.

2.3. Battery assembling and electrochemical test

The as-synthesized MnO_2 -SS cathode was cut into a disc with the diameter of 16 mm and then directly used as cathode electrodes for the Li– O_2 battery. The cathode performance was characterized based on a home-made lithium–oxygen battery composed of a Li metal anode (15.8 mm in diameter, 0.45 mm in thickness), a glass-fiber separator (GF/C, Whatman), and the MnO_2 -SS cathode. The electrolyte is 1.0 M lithium perchlorate (LiClO_4 , battery grade, Sigma–Aldrich) in dimethyl sulfoxide (DMSO, $\geq 99.9\%$, Sigma–Aldrich), which was dried with molecular sieves before use. Being assembled in an Ar-filled glove box system (Etelux, Lab 2000) with

oxygen and water contents below 1 ppm, the battery was operated with pure O_2 at a constant pressure of 1.25 atm.

The galvanostatic charge and discharge tests were conducted on a battery test system (Neware, CT-3008 W) at current densities of 0.1, 0.2, 0.3 mA cm^{-2} with a lower voltage limit of 2.0 V. To investigate the charge performance, the charge capacity was set to be equal to the discharge capacity with an upper voltage limit of 4.6 V. All tests were carried out at the ambient temperature (25 ± 0.5 $^\circ\text{C}$) after a 2 h rest period. To eliminate the effect of oxygen on the lithium anode [29], a LiFePO_4 (anode side)/ MnO_2 -SS (cathode side) lithium ion–oxygen battery was discharged and charged at the current density of 0.2 mA cm^{-2} with a fixed specific capacity of 500 $\text{mA h g}_{\text{MnO}_2}^{-1}$.

3. Results and discussion

3.1. Morphology and crystal structure of the MnO_2 -SS electrode

Fig. 1 shows the morphologies of the SS substrate and the MnO_2 -SS cathode. Before the MnO_2 deposition, the surface of the SS fiber is clean and smooth (see Fig. 1a), but after deposition the surface is covered by a layer of MnO_2 (Fig. 1b). The thickness of the MnO_2 layer on the SS is estimated to be 8.0 μm , measured at the location of damage (Fig. 1c). After several discharge/charge cycles, the cathode was washed with a solution of 0.1 M H_2SO_4 and H_2O_2 to investigate the surface of the SS fiber. The result shows that there is no change to the surface morphology (Fig. 1d), indicating that there is no corrosion of SS fiber occurring during the charge–discharge cycles.

To clarify the valence state of Mn, the XPS spectra are recorded and shown in Fig. 2. From the XPS peaks of Mn2p, it is found that the peaks of Mn2p_{1/2} and Mn2p_{3/2} are located at about 642.4 eV and 654.1 eV. The difference between them is approximately 11.7 eV, indicating that the main product deposited on the SS substrates is MnO_2 [30]. Meanwhile, from the XRD patterns as shown in the inset of Fig. 2, the MnO_2 powder collected from the MnO_2 -SS shows a broad diffraction peak between 20 $^\circ$ and 30 $^\circ$. These observations suggest that the manganese oxide on the SS substrate is the amorphous MnO_2 .

3.2. Electrochemical property of the MnO_2 -SS electrode

Fig. 3 shows the discharge/charge curves of different cathodes in Ar and O_2 at 0.1 mA cm^{-2} . The MnO_2 -SS electrode in O_2 exhibits a capacity of 3.562 mA h, but the capacity is as low as 0.098 mA h in Ar. The comparison between capacity in O_2 and that of Ar indicates that the discharge capacity of the Li– O_2 battery mainly results from the ORR on the MnO_2 -SS electrode. Furthermore, the SS electrode without MnO_2 only results in a capacity of as low as 0.034 mA h in O_2 , suggesting that the SS fiber has no catalytic activity for ORR in the Li– O_2 battery and the capacity achieved is attributed to the MnO_2 layer.

The effect of current density on the discharge/charge voltage of the Li– O_2 battery with the MnO_2 -SS cathode is shown in Fig. 4. At the current density of 0.1 mA cm^{-2} (100 $\text{mA h g}_{\text{MnO}_2}^{-1}$), the Li– O_2 battery with the MnO_2 -SS cathode can deliver a specific capacity of 1781 $\text{mA h g}_{\text{MnO}_2}^{-1}$, which is comparable to that of the Co_3O_4 -Ni foam electrode (1880 $\text{mA h g}_{\text{Co}_3\text{O}_4}^{-1}$) [19]. All the capacities can be charged with the charge voltage under 4.4 V. At higher current densities of 0.2 mA cm^{-2} and 0.3 mA cm^{-2} , the specific discharge capacities reach 1242 $\text{mA h g}_{\text{MnO}_2}^{-1}$ and 625 $\text{mA h g}_{\text{MnO}_2}^{-1}$, with the charge voltages of 4.47 V and 4.55 V, respectively.

To examine the stability of the MnO_2 -SS electrode, a LiFePO_4 (anode side)/ MnO_2 -SS (cathode side) lithium ion–oxygen battery was tested with a fixed specific capacity of 500 $\text{mA h g}_{\text{MnO}_2}^{-1}$ at the

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