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A non-carbon cathode electrode for lithium-oxygen batteries

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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.

ARTICLE INFO	ABSTRACT
Article history: Received 29 March 2014	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,
Received in revised form 7 May 2014 Accepted 15 May 2014 Available online 6 June 2014 Keywords:	we propose and fabricate a non-carbon cathode electrode consisting of MnO ₂ -deposited stainless steel (SS) felts. Amorphous MnO ₂ layer are electrodeposited on the surfaces of SS fibers at an anodic current
	in a manganese acetate solution. The use of the MnO_2 -SS electrode in a non-aqueous lithium-oxygen battery delivers a specific capacity of 1780 mA b g^{-1} . Furthermore, the discharge/charge cycle test with
	a fixed capacity of 500 mA h $g_{Mn0_2}^{-1}$ shows that this electrode can discharge/charge for more than 10 cycles

ising electrode for high-performance lithium-oxygen batteries.

without degradation. It is, therefore, expected that this novel non-carbon and stable cathode is a prom-

Keywords: Li-O₂ batteries Non-carbon cathode MnO2-stainless steel

1. Introduction

Due to its high capacity and high energy density, the lithiumoxygen $(Li-O_2)$ 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 lithiumoxygen 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:

$$2(Li^{+} + e^{-}) + O_2 \xrightarrow{\text{discharge} \\ \text{charge}} Li_2O_2$$
(1)

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.

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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 lithiumoxygen battery with dimethyl sulfoxide (DMSO) as the electrolyte





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[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 MnO₂ layer as the catalyst. The following features of the new cathode are expected: (i) as this non-carbon cathode can avoid irreversible Li₂CO₃-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) MnO₂ 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 ($C_4H_6MnO_4 \cdot 4H_2O$, 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·H₂SO₄ solution, rinsed with distilled water (DI) and acetone, and then air-dried. 6.0 cm² of SS felt was then immersed in the solution containing 0.5 M Na₂SO₄ and C₄H₆MnO₄ to be used as the cathode. The other piece of clean SS felt was used as the anode. The MnO₂ 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 °C for 12 h. The mass of MnO₂ film was controlled to be 1.0 mg cm⁻² by adjusting the electrodepositing 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 MnO₂ electrode were analyzed with a Philips high resolution X-ray diffraction system (model PW1825) using a Cu K α source operating at 40 keV.

2.3. Battery assembling and electrochemical test

The as-synthesized MnO₂–SS cathode was cut into a disc with the diameter of 16 mm and then directly used as cathode electrodes for the Li–O₂ 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 MnO₂–SS cathode. The electrolyte is 1.0 M lithium perchlorate (LiClO₄, 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 °C) after a 2 h rest period. To eliminate the effect of oxygen on the lithium anode [29], a LiFePO₄ (anode side)/MnO₂–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 mA h $g_{MnO_2}^{-1}$.

3. Results and discussion

3.1. Morphology and crystal structure of the MnO₂–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 H₂SO₄ and H₂O₂ 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 Mn2p1/2 and Mn2p3/2 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 MnO₂ [30]. Meanwhile, from the XRD patterns as shown in the inset of Fig. 2, the MnO₂ powder collected from the MnO₂–SS shows a broad diffraction peak between 20° and 30°. These observations suggest that the manganese oxide on the SS substrate is the amorphous MnO₂.

3.2. Electrochemical property of the MnO₂-SS electrode

Fig. 3 shows the discharge/charge curves of different cathodes in Ar and O_2 at 0.1 mA cm⁻². The MnO₂–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 MnO₂–SS electrode. Furthermore, the SS electrode without MnO₂ 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 MnO₂ layer.

The effect of current density on the discharge/charge voltage of the Li–O₂ battery with the MnO₂–SS cathode is shown in Fig. 4. At the current density of 0.1 mA cm⁻² (100 mA h $g_{MnO_2}^{-1}$), the Li–O₂ battery with the MnO₂–SS cathode can deliver a specific capacity of 1781 mA h $g_{MnO_2}^{-1}$, which is comparable to that of the Co₃O₄–Ni foam electrode (1880 mA h $g_{C_3O_4}^{-1}$) [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 mA h $g_{MnO_2}^{-1}$ and 625 mA h $g_{MnO_2}^{-1}$, with the charge voltages of 4.47 V and 4.55 V, respectively.

To examine the stability of the MnO₂–SS electrode, a LiFePO₄ (anode side)/MnO₂–SS (cathode side) lithium ion-oxygen battery was tested with a fixed specific capacity of 500 mA h $g_{\rm MO_2}^{-1}$ at the



Fig. 1. SEM and EDX images: (a) bare SS felt; (b and c) MnO₂-SS; (d) SS felt after cycles; and (e and f) EDS mapping of O, Mn of the MnO₂-SS electrode, respectively.



Fig. 2. XPS patterns of the MnO_2 for Mn2p. Inset: XRD patterns of the MnO_2 .

current density of 0.2 mA cm⁻² (200 mA h $g_{MnO_2}^{-1}$). Before the cycling test, the LiFePO₄ electrode was pretreated according to the procedures reported in the literature [31]. The discharge/ charge voltage versus LiFePO₄ is converted to the potential versus



Fig. 3. Discharge/charge performance of the bare SS felt and MnO_2 -SS cathode. Inset: detail of bare SS felt in O_2 and MnO_2 -SS cathode in Ar.

lithium metal, and the result is shown in Fig. 5. It can be found that the discharge potential decreases with cycles, whereas the charge potential increases slightly. This phenomenon may result from the decomposition of the DMSO solvent. DMSO has been used as



Fig. 4. Discharge/charge performance of the $\rm MnO_2\text{-}SS$ cathode at different current densities.



Fig. 5. Cycle performance of the MnO₂-SS electrode.

the electrolyte in Li–O₂ batteries for many cases, but there may still be some gas phase product from its decomposition [18]. To prove this assumption, the oxygen gas in the cathode compartment was replaced with fresh oxygen at the end of charge process of the 10th cycle, and the discharge potential of the 11th cycle is recovered to 2.842 V_{vs Li}, close to the first cycle (2.869 V_{vs Li}) and much higher than the 10th cycle (2.314 V_{vs Li}). This shows that the MnO₂–SS electrode has very good stability for cycles.

4. Conclusions

In this work, we have proposed a MnO_2 -SS cathode electrode for the non-aqueous lithium–oxygen battery. The deposition of MnO_2 onto the SS felt is achieved by a simple anodic electrodeposition method. The most striking feature of this electrode is that it does not contain carbon, alleviating the corrosion problem in conventional carbon-based electrodes. The use of MnO_2 as the catalyst for both ORR and OER enabled a specific capacity of 1781 mA h $g_{MnO_2}^{-1}$ at the current density of 0.10 mA cm⁻², with the charge voltage under 4.4 V. The cycle performance was tested with a constructed LiFePO₄ (anode side)/MnO₂-SS-oxygen (cathode side) battery and the result showed a good stability of the proposed electrode. The above described facts suggest that the MnO₂–SS cathode developed in this work is a cheap and promising electrode for non-aqueous lithium–oxygen batteries.

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