available at www.sciencedirect.com

journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue on Electrocatalysis Transformation)

A binder-free, flexible cathode for rechargeable Na-O₂ batteries

Na Li ^{a,b}, Dan Xu ^{a,b}, Di Bao ^{a,b}, Jinling Ma ^{a,b}, Xinbo Zhang ^{a,b,*}^a State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, Jilin, China^b University of Chinese Academy of Sciences, Beijing 100049, China

ARTICLE INFO

Article history:

Received 25 January 2016

Accepted 29 March 2016

Published 5 July 2016

Keywords:

Flexible

Binder-free

Cobalt oxide nanowires

Porosity

Catalytic activity

ABSTRACT

Rechargeable Na-O₂ batteries have attracted significant attention as energy storage devices owing to their theoretically high energy storage capacity and the natural abundance of sodium. However, practical applications of this type of battery still suffer from low specific capability, poor cycle stability, instable electrolytes, and unstable polymer binders. Herein, we report a facile method of synthesizing binder free and flexible cathodes with Co₃O₄ nanowire arrays vertically grown onto carbon textiles. When employed as a cathode for Na-O₂ batteries, this cathode exhibits superior performance, including a reduction of charge overpotential, high specific capacity (4687 mAh/g), and cycle stability up to 62 cycles. These enhanced performance can be attributed to the synergistic effect of the porosity and catalytic activity of the Co₃O₄ nanowire catalyst.

© 2016, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Rechargeable metal-air batteries have attracted significant attention as energy storage devices owing to their higher theoretical energy density than commercialized Li-ion batteries, especially non-aqueous Li-O₂ and Na-O₂ batteries [1–6]. Na-O₂ batteries are of particular interest as Na exhibits similar physicochemical properties to Li. Considering the limited Li resources that are inadequate to satisfy the increasing demand for batteries based on Li chemistry, many researchers call for using Na to replace Li owing to its abundance and inexpensive nature [7–9]. However, before the practical application of Na-O₂ batteries becomes a reality many significant technical challenges need to be overcome, such as poor rate capacities, low round trip efficiencies (caused by a high overpotential of both the oxygen reduction reaction (ORR) and oxygen evolu-

tion reaction (OER)), unstable electrolytes and polymer binders (which undergo side reactions), and short cycle lives [10,11]. And, similar to Li-O₂ batteries, the properties of the cathode material (such as morphology, specific surface area, structure, activity, and conductivity) play an important role in the performance of Na-O₂ batteries [12–15]. In response, many scientists have tried to overcome these above mentioned limitations by finding a suitable cathode catalyst to accelerate the ORR and OER kinetics of rechargeable Na-O₂ batteries. They tried to achieve this by adjusting the porous structure of the cathode catalyst to improve cycle stability through providing enough paths for oxygen and ion migration and enough sites for deposition of the discharge product. Additionally, researchers have tried tailoring the cathode structure to enhance its structural stability [16]. For example, carbon supported catalysts, such as mesoporous carbon, carbon fiber, and N-doped graphene

* Corresponding author. Tel/Fax: +86-431-85262235; E-mail: xzbzhang@ciac.ac.cn

This work was supported by the 100 Talents Programme of the Chinese Academy of Sciences, the National Basic Research Program of China (973 Program, 2014CB932300, 2012CB215500), and the National Natural Science Foundation of China (21422108, 51472232, 51301160).

DOI: 10.1016/S1872-2067(15)61089-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 7, July 2016

nanosheets have been widely used as cathodes for Na-O₂ batteries owing to their enhanced electronic conductivity and catalytic activity [17–19]. In general, cathodes are prepared by coating a homogenous slurry containing conductive carbon powder, polymer binder (e.g. PVDF and PTFE), and catalyst onto the current collector. However, the carbon itself and the commonly used polymer binder are reported to be unstable, forming decomposition products during the discharge/charge process [20,21]. To solve these problems, the development of a binder free or non-carbon cathode is of great importance. Prioritizing the mechanical strength of the cathode, we chose carbon textiles as the base owing to their superior flexibility and excellent electrochemical stability.

Herein, we report a facile and efficient hydrothermal synthesis method to fabricate a flexible and binder free cathode with Co₃O₄ nanowire arrays vertically grown onto carbon textiles (this cathode is referred to as COCT throughout the rest of this manuscript). When employed as cathode in a Na-O₂ battery, the COCT cathode endows the Na-O₂ battery with lower overpotential, enhanced specific capacity of 4687 mAh/g (based on weight of Co₃O₄), and enhanced cycling performance (62 cycles).

2. Experimental

2.1. Material preparation

Co(NO₃)₂·6H₂O and NH₄F were purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Urea (CO(NH₂)₂), tetraethylene glycol dimethyl ether (TEGDME), and sodium triflate (NaCF₃SO₃) were purchased from Aladdin Reagent. Carbon textiles (CT) were purchased from Torray.

The COCT cathode was synthesized using a hydrothermal method. The CTs were ultrasonically cleaned several times with acetone, absolute ethanol, and distilled water and then dried at 60 °C in a vacuum oven for 12 h. The precursor solutions were obtained by dissolving a desired amount of mixed salt (the molar ration of Co(NO₃)₂·6H₂O:NH₄F:CO(NH₂)₂ = 1:1:2) into 40 mL distilled water at room temperature. After stirring for 1 h, the above solutions were transferred to a Teflon lined stainless steel autoclave (50 mL) and the cleaned CTs were immersed in the precursor solutions. Then the Teflon lined stainless steel autoclaves were heated at 120 °C for 5 h in an oven. After cooling down, the CTs were removed from the autoclaves and rinsed several times with deionized water and ethanol, then dried in a vacuum oven at 120 °C for 12 h. Finally,

the samples were annealed in air at 400 °C for 2 h. The synthesis steps for COCT cathodes are schematically illustrated in Scheme 1.

2.2. Characterization

Powder X-ray diffraction (XRD) measurements were performed with a Bruker D8 Focus Powder X-ray diffractometer using Cu K_α radiation (40 kV, 40 mA). Scanning electron microscopy (SEM) was performed using a HITACHI S-4800 field mission scanning electron microscope. Transmission electron microscopy (TEM) and high resolution transmission electron microscopy (HRTEM) were undertaken on a FEI Tacnai G2 electron microscope operated at 200 kV. X-ray photoelectron spectroscopy (XPS) analysis was carried on a VG Scientific ESCALAB MKII X-ray photoelectron spectrometer.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were performed on a Bio-Logic VMP3 electrochemical workstation. Na-O₂ battery measurements were cycled on a LAND CT2001AS2 multi-channel battery testing system.

2.3. Na-O₂ battery preparation and electrochemical performance measurements

The electrochemical performance of COCT as a cathode in a Na-O₂ battery was tested using a coin2025 type cell. The cathodes were dried in a vacuum oven at 80 °C for 24 h. All batteries were assembled in a glove box under Ar atmosphere, using a sodium metal foil anode, glass fiber separator, oxygen cathode, and electrolyte containing 0.5 mol/L NaCF₃SO₃ in TEGDME. Galvanostatic discharge-charge tests were conducted within a voltage window of 1.8–4.2 V (vs. Na/Na⁺) at ambient temperature after a 2–5 h rest period. EIS measurements of the cells were carried out using an AC impedance analyzer within a frequency range of 10⁶ to 10^{−2} Hz. The CV curves were measured from 1.8 to 4.0 V at a voltage sweep rate of 0.5 mV/s.

3. Results and discussion

3.1. Materials characterization

We investigated the morphology and structure of the COCT cathode using SEM and TEM. Fig. 1(a) shows an SEM image of the pristine CT, revealing that the CTs are woven by carbon fibers with diameters of about 10 μm. Fig. 1(b) and (c) show

Scheme 1. Schematic illustration of the formation of Co₃O₄ NWs/carbon textiles composite.

SEM images at different magnifications of the carbon textiles after Co_3O_4 NWs were grown on them; it could be observed that the Co_3O_4 NWs vertically grew uniformly on the CT frame without the help of any additional polymeric binder. This contributes to the formation of a low resistance path for electron transport. The average diameter of the nanowires was about 40 nm (Fig. 1(d)). The HRTEM image collected from the surface of the Co_3O_4 NWs exhibits well resolved lattice fringes with d spacings of 0.24 and 0.47 nm, corresponding to the (311) and (111) planes of Co_3O_4 , respectively (Fig. 1(e)). The selected area electron diffraction (SAED) pattern shown in the inset of Fig. 1e demonstrates the polycrystalline nature of the NWs. Moreover, the XRD pattern (Fig. 1(f)) shows that the diffraction peaks can be assigned to the crystalline Co_3O_4 phase (JCPDS 42-1467).

Further, no other diffraction peaks were observed, which confirms that there were no impurities.

To examine the elemental distribution and composition of the COCT surface, we used energy dispersive spectrometer (EDS) mapping (Fig. 2(a)–(e)). O and Co are uniformly distributed around a single CT fiber, and the diameter is increased from 10 μm (pure CT fiber) to about 13 μm for the resulting composite COCT. The SEM and EDS images demonstrate the core-shell configuration of COCT, so this structure can effectively prevent the carbon textiles from decomposing. A more detailed elemental composition and the oxidation state of the Co_3O_4 NWs are measured by XPS. From the C 1s spectra (Fig. 2(f)), we can see that C is not oxidized (the standard binding energy of C 1s is 285.0 eV). By using a Gaussian fitting method

Fig. 1. (a) SEM image and photograph (inset) of pristine carbon textiles. SEM image and photograph (inset) of the obtained carbon textiles/ Co_3O_4 NWs (COCT) cathode at (b) low-magnification and (c) high-magnification. (d) TEM image, (e) HRTEM image and SADE (inset) image of Co_3O_4 NWs. (f) XRD patterns of the COCT cathode.

Fig. 2. (a) TEM image of COCT cathode. (b) All three elements in the composite and corresponding elemental mapping images of (c) C, (d) O, and (e) Co. XPS spectra of the (f) C 1s and (g) Co 2p peaks.

the best deconvolution of the Co 2p profile was achieved, which showed two pairs of spin-orbit doublets indicating the existence of Co^{2+} and Co^{3+} , which is consistent with previously published results on Co_3O_4 (Fig. 2(g)) [22,23].

Compared with the traditional air cathode, this flexible electrode material exhibits many advantageous properties that are vital to the transportation of oxygen, electrons, and ions, and thus improves the electrochemical performance of Na- O_2 batteries. More importantly, Co_3O_4 NWs are vertically grown onto carbon textiles without the help of any polymeric binder, thereby effectively reducing the resistance of the cathode and avoiding side reactions originating from the decomposition of the non-conductive polymeric binder. Finally, the flexibility of the COCT cathode paves the way for the practical application of flexible Na- O_2 battery devices.

3.2. Electrochemical performance of Na- O_2 battery

The electrochemical performance of COCT cathodes compared with pure CT cathodes and with Co_3O_4 pasted on CT (CO@CT) cathodes was examined in Na- O_2 batteries. We choose TEGDME (because of its relatively high stability toward O_2) with NaCF_3SO_3 as the electrolyte [24,25]. The discharge-charge curves of the Na- O_2 batteries with the three different cathodes are shown in Fig. 3(a). The overpotential of the

Na- O_2 batteries with the COCT cathode is lower than for the other two cathodes. We found that the discharge specific capacity and charge-discharge voltage was improved by the Co_3O_4 NWs. Specifically, the discharge capacity of the COCT cathode was 4687.2 mAh/g, which is three times that of the CO@CT cathode (1533.4 mAh/g). We attribute this to more void space being available for the deposition of discharge products and to the binder free character of the COCT cathode (polymer binder usually decomposes). The capacity of the Na- O_2 battery with the pure CT cathode is 1113.7 mAh/g, which is almost one-fourth that of the cell with the COCT cathode. The discharge voltage and charge voltage of the COCT devices indicate that the Co_3O_4 NWs have superior ORR and OER catalytic activity. Furthermore, to exclude possible electrochemical contributions from intercalation reactions with CT and/or Co_3O_4 NWs, we investigated the CV curves of Na- O_2 batteries (Fig. 3(b)). Compared with the CT cathode, the COCT cathode exhibits a higher ORR onset potential and ORR/OER peak current, which indicates the Co_3O_4 NWs have excellent catalytic activity. The enhanced ORR/OER kinetics could lead to improvements in the energy output, recharging characteristics, and round trip efficiency of the Na- O_2 batteries.

Inspired by the superior catalytic activity of Co_3O_4 NWs, we further examined the energy efficiency of Na- O_2 batteries. We found that the COCT cathode had a higher discharge capacity

Fig. 3. (a) First discharge-charge curves of Na- O_2 batteries at a current density of 100 mA/g. (b) CV curves of Na- O_2 batteries with CT and COCT cathodes (scan rate: 0.1 mV/s). Comparison of (c) discharge specific capacity and (d) capacity retention capability of CT and COCT cathodes at different current densities.

(Fig. 3(c)) and capacity retention rate (Fig. 3(d)) at both 100 mA/g and 1000 mA/g current density compared with the pure CT cathode, which we attribute to a synergistic effect of increased catalytic activity and increased porosity of the Co_3O_4 NWs. To clarify the above point, we investigated the SEM images of these two kinds of cathodes (Fig. 4). The discharge products on the CT cathode were shaped like sheets (Fig. 4(c)), while the discharge products grown on the Co_3O_4 NWs were uniformly distributed on the COCT cathode (Fig. 4(d)). The porous Co_3O_4 NWs provide enough space for the deposition of the discharge products, thereby resulting in a high discharge specific capacity. In addition, the Co_3O_4 NWs offer more oxygen and electrolyte paths in the electrode, which is crucial to improve the rate capability, as reported in other types of metal-air batteries.

Additionally, another enhancement of Na- O_2 batteries with COCT cathodes is their increased cycling stability. As shown in Fig. 5(a) and (b), the batteries with COCT cathodes can cycle for 62 cycles at a current density of 100 mA/g with the limited capacity of 500 mAh/g, compared with the pure CT cathode with only 16 cycles. This enhanced cycling stability may be attributed to the unique properties of the COCT cathode because its ordered, porous Co_3O_4 electrocatalyst NWs may accelerate the formation and decomposition of the discharge products thereby improving the rechargeability of the cathode. Evidence for this is found in the SEM images (Fig. 4) of cathode:

Fig. 4. SEM images of CT cathode and COCT cathode. (a, b) Pristine; (c, d) After discharged; (e, f) After recharged state. The current density was 100 mA/g.

Fig. 5. Discharge-charge curves of Na- O_2 batteries with (a) CT and (b) COCT cathodes at a current density of 100 mA/g with the limited specific capacity of 500 mAh/g. EIS of Na- O_2 batteries with (c) CT and (d) COCT cathodes at different discharge/charge stages.

Fig. 6. XRD patterns of (a) CT and (b) COCT cathodes.

the discharge products on the CT cathode were shaped like sheets (Fig. 4(c)), while they formed a film on the Co_3O_4 NWs (Fig. 4(d)). After recharge, the discharge products completely decompose on the COCT cathode (Fig. 4(f)), indicating the recovery of COCT cathode, which ensures the rechargeability of the batteries. Conversely, the discharge products incompletely decomposed on the pure CT cathode. We investigated the different electrochemical characteristics affecting charge efficiencies of the cathodes using EIS of both CT and COCT cathode Na-O_2 batteries at different discharged/charged states. As shown in Fig. 5(c) and (d), we found that the impedances of pure CT and COCT Na-O_2 batteries in the pristine state are almost the same. After discharge, the impedances of both batteries increased significantly, which was caused by the poor electronic conductivity of the discharge products generated on the cathode. Interestingly, the impedances of Na-O_2 batteries with COCT cathodes can almost be restored to the pristine state (Fig. 5(d)) after being recharged, which indicates that the discharge products can be almost fully decomposed during the charging process; this conclusion is in agreement with the findings from the SEM images of the COCT cathode (Fig. 4(f)). Conversely, the impedance of Na-O_2 batteries with pure CT cathodes increases monotonously during the charging processes (Fig. 5(b)) owing to the incomplete decomposition of the discharge products (Fig. 4(e))—this once again highlights the unique properties of COCT cathodes.

Based on the thermodynamic standard potential of different sodium oxides and considering the real discharge voltage and the similar standard potentials, we deduce that the most likely discharge products are Na_2O_2 or NaO_2 or a mixture of Na_2O_2 and NaO_2 :

To understand the discharge products of our Na-O_2 batteries, we investigated the cathode surface using XRD. As shown in Fig. 6, both of the XRD patterns reveal that the composition of discharge products is a mixture of NaO_2 and Na_2O_2 . The peaks associated with these discharge products appeared after discharging and vanished after recharging, which is consistent

with the SEM images and EIS data, demonstrating the reversibility of our Na-O_2 batteries. Specifically, the XRD peaks associated with the COCT cathode were weaker than those of the CT cathode, indicating the poor crystallinity of the discharge products, which causes a high specific capacity and cycling stability of the batteries. After recharging, the XRD peaks of the discharge products on the COCT cathode vanished, indicating that the products completely decomposed, which is in agreement with the EIS results (Fig. 5(f)) and SEM images (Fig. 4(d)).

4. Conclusions

In summary, we demonstrated a facile and efficient method of fabricating a flexible binder free COCT cathode. When directly employed as the O_2 cathode, Na-O_2 batteries exhibit high specific capacity and enhanced cycling stability, which was attributed to the enhanced catalytic activity, porous nature, and flexible binder free structure of the COCT cathode. Although flexible power sources are crucial for the realization of next-generation flexible electronics, their application in such devices is hindered by their low theoretical energy density. Therefore, flexible Na-O_2 batteries with COCT cathodes show great potential. However, to develop Na-O_2 batteries for practical device applications, enormous challenges and technological issues must still be overcome, such as protecting the sodium and eliminating side reactions.

References

- [1] P. G. Bruce, S. A. Freunberger, L. J. Hardwick, J. M. Tarascon, *Nat. Mater.*, **2012**, 11, 19–29.
- [2] Z. Q. Peng, S. A. Freunberger, Y. H. Chen, P. G. Bruce, *Science*, **2012**, 337, 563–566.
- [3] P. Hrtmann, C. L. Bender, M. Vracar, A. K. Duerr, A. Garsuch, J. Janek, P. Adelhelm, *Nat. Mater.*, **2013**, 12, 228–232.
- [4] C. L. Bender, P. Hartmann, M. Vracar, P. Adelhelm, J. Janek, *Adv. Energy Mater.*, **2014**, 4, 1301863/1–1301863/10.
- [5] T. Zhang, H. S. Zhou, *Nat. Commun.*, **2013**, 4, 2855.
- [6] Z. L. Wang, D. Xu, J. J. Xu, X. B. Zhang, *Chem. Soc. Rev.*, **2014**, 43, 7746–7786.
- [7] N. Zhao, C. L. Li, X. X. Guo, *Phys. Chem. Chem. Phys.*, **2014**, 16,

Graphical Abstract

Chin. J. Catal., 2016, 37: 1172–1179 doi: 10.1016/S1872-2067(15)61089-0

A binder-free, flexible cathode for rechargeable Na-O₂ batteries

Na Li, Dan Xu, Di Bao, Jinling Ma, Xinbo Zhang*

Changchun Institute of Applied Chemistry, Chinese Academy of Sciences;
University of Chinese Academy of Sciences

Co₃O₄ NWs grow on the carbon textiles via hydrothermal and thermal treatment processes, which can be used as flexible and binder free cathodes for Na-O₂ batteries. The discharge products consist of NaO₂ and Na₂O₂.

- 15646–15652.
- [8] S. P. Zhang, Z. Y. Wen, K. Rui, C. Shen, Y. Lu, J. H. Yang, *J. Mater. Chem. A*, **2015**, 3, 2568–2571.
 - [9] J. Kim, H. D. Lim, H. Gwon, K. Kang, *Phys. Chem. Chem. Phys.*, **2013**, 15, 3623–3629.
 - [10] X. X. Bi, X. D. Ren, Z. J. Huang, M. Z. Yu, E. Kreidler, Y. Y. Wu, *Chem. Commun.*, **2015**, 51, 7665–7668.
 - [11] Y. X. Hu, X. P. Han, Q. Zhao, J. Du, F. Y. Cheng, J. Chen, *J. Mater. Chem. A*, **2015**, 3, 3320–3324.
 - [12] J. J. Xu, Z. L. Wang, D. Xu, L. L. Zhang, X. B. Zhang, *Nat. Commun.*, **2013**, 4, 2438.
 - [13] J. J. Xu, D. Xu, Z. L. Wang, H. G. Wang, L. L. Zhang, X. B. Zhang, *Angew. Chem. Int. Ed.*, **2013**, 52, 3887–3890.
 - [14] Z. Y. Guo, D. D. Zhou, X. L. Dong, Z. J. Qiu, Y. G. Wang, Y. Y. Xia, *Adv. Mater.*, **2013**, 25, 5668–5672.
 - [15] H. Yadegari, M. N. Banis, B. W. Xiao, Q. Sun, X. Li, A. Lushington, B. Q. Wang, R. Y. Li, T. K. Sham, X. Y. Cui, X. L. Sun, *Chem. Mater.*, **2015**, 8, 3040–3047.
 - [16] W. W. Yin, Z. Shadike, Y. Yang, F. Ding, L. Sang, H. Li, Z. W. Fu, *Chem. Commun.*, **2015**, 51, 2324–2327.
 - [17] W. J. Kwaka, Z. H. Chen, C. S. Yoon, J. K. Lee, K. Amine, Y. K. Sun, *Nano Energy*, **2015**, 12, 123–130.
 - [18] Y. L. Li, H. Yadegari, X. F. Li, M. N. Banis, R. Y. Li, X. L. Sun, *Chem. Commun.*, **2013**, 49, 11731–11733.
 - [19] W. Liu, Q. Sun, Y. Yang, J. Y. Xie, Z. W. Fu, *Chem. Commun.*, **2013**, 49, 1951–1953.
 - [20] W. M. Liu, W. W. Yin, F. Ding, L. Sang, Z. W. Fu, *Electrochem. Commun.*, **2014**, 45, 87–90.
 - [21] Y. M. Cui, Z. Y. Wen, Y. Liu, *Energy Environ. Sci.*, **2011**, 4, 4727–4734.
 - [22] T. Y. Ma, S. Dai, M. Jaroniec, S. Z. Qiao, *J. Am. Chem. Soc.*, **2014**, 136, 13925–13931.
 - [23] W. Xia, R. Q. Zou, L. An, D. G. Xia, S. J. Guo, *Energy Environ. Sci.*, **2015**, 2, 568–576.
 - [24] B. D. McCloskey, D. S. Bethune, R. M. Shelby, G. Girishkumar, A. C. Luntz, *J. Phys. Chem. Lett.*, **2011**, 2, 1161–1166.
 - [25] Y. C. Lu, D. G. Kwabi, K. P. C. Yao, J. R. Harding, J. G. Zhou, L. Zuind, S. H. Yang, *Energy Environ. Sci.*, **2011**, 4, 2999–3007.

一种无粘结剂的柔性正极材料用于可充电的钠空气电池

李娜^{a,b}, 徐丹^{a,b}, 鲍迪^{a,b}, 马金玲^{a,b}, 张新波^{a,b,*}

^a中国科学院长春应用化学研究所稀土资源利用国家重点实验室, 吉林长春130022

^b中国科学院大学, 北京100049

摘要: 随着全球环保意识的加强, 开发具有环保可持续且高能量密度的能源逐渐成为人们关注的焦点。近年来, 金属-空气电池凭借其高的能量密度作为能源存储器件已经引起了人们的广泛关注。最重要的是, 此类电池的反应物为空气中的氧气, 并不需要辅助设备对其储存, 使得无论在质量和体积方面均优于其他二次电池。尤其锂空气电池凭借其高的理论比容量 11140 Wh/kg, 比现有锂离子电池高出 1–2 个数量级, 且有质量轻便等优势, 成为近几年的研究热点。然而, 考虑到金属锂资源的短缺和金属钠与其具有相似的物理化学性质, 因此呼吁用金属钠取代金属锂, 钠-空气电池作为未来的储能器件引起了广大研究者的兴趣。但是, 钠空气电池目前的实际应用仍存在很多问题: 充放电过程中产生过高的过电位, 循环寿命低, 电解液不稳定, 粘结剂的不稳定性, 空气正极的结构以及外界操作环境条件等。解决问题的一种重要途径就是寻找合适的催化剂和设计合理的电极结构。催化剂的加入既可以增强其氧还原 (ORR) 及氧析出 (OER) 活性又可以通过调控电极的结构, 为氧气、电子和离子的运输提供更多的通道, 从而加速 ORR 和 OER 进程。基于粘结剂的不稳定性, 需设计一体化的正极材料。由于碳纤维布作为柔性集流体具有高的机械强度和电化学稳定性好的优点, 因此本文使用水热处理和热处理两步法在碳纤维布上原位生长 Co₃O₄ 纳米线 (Co₃O₄ NWs), 制备柔性、无粘结剂的一体化正极材料 (COCT) 用于

钠空气电池. 本实验以硝酸钴为主盐, 尿素为矿化剂, 氟化铵为络合剂, 通过 120 °C 热处理 5 h 在碳纤维布上生长 Co_3O_4 NWs 的前驱体, 然后经过 400 °C 热处理 2 h 得到一体化柔性电极材料并用于钠空气电池, 该材料表现出优异的电化学性能: 充放电过程产生较低的过电位; 高的放电比容量 4687 mAh/g, 碳纤维布作为正极放电容量是 1113.7 mAh/g; 能稳定循环 62 圈 (碳纤维布作为正极循环 16 圈). 这些优异的性能可归功于 Co_3O_4 NWs 高的催化性能和多孔性效应: (1) 由于 Co_3O_4 NWs 紧密地附着在碳纤维布表面, 形成了快速的电子传导通道, 因而具有优异的电子传导性; (2) Co_3O_4 NWs 之间的空隙以及多孔结构增加了反应的活性面积和活性位点, 这种结构有利于氧气和离子的运输以及电解液的扩散, 从而加速 ORR 和 OER 进程; (3) COCT 电极结构能为放电产物和反应物提供更多的存储位置, 从而提高了放电容量和倍率性能. 结果证实, 钠空气电池的放电产物是过氧化钠和超氧化钠的混合物. 加入催化剂后, 放电产物的形貌发生了变化: 当碳纤维布作为正极材料时, 放电产物的形貌是片状的; COCT 电极作为正极材料时, 放电产物沿着 Co_3O_4 NWs 生长. 这种柔性一体化正极材料的应用, 为柔性钠空气电池器件的发展起到了巨大的推动作用.

关键词: 柔性; 无粘结剂; 四氧化三钴纳米线; 多孔性; 催化性能

收稿日期: 2016-01-25. 接受日期: 2016-03-29. 出版日期: 2016-07-05.

*通讯联系人. 电话/传真: (0431)85262235; 电子信箱: xbzhang@ciac.ac.cn

基金来源: 中国科学院百人计划; 国家重点基础研究发展计划 (973 计划, 2003CB615804, 2012CB215500); 国家自然科学基金 (21422108, 51472232, 51301160).

本文的英文电子版由 Elsevier 出版社在 ScienceDirect 上出版 (<http://www.sciencedirect.com/science/journal/18722067>).