

# MnO<sub>2</sub> Nanotubes Synthesized with One-step Hydrothermal Method as Efficient Bi-functional Cathode Catalyst for a Rechargeable Zinc–air Battery

Haoran Li<sup>1</sup>, Xuemei Li<sup>1</sup>, Qi Nie<sup>1</sup>, Keryn Lian<sup>2</sup> and Jinli Qiao<sup>1,\*</sup>

<sup>1</sup>College of Environmental Science and Engineering, Donghua University,  
2999 Ren'min North Road, Shanghai 201620, China

<sup>2</sup>Department of Materials Science and Engineering., University of Toronto,  
Toronto, Ontario, Canada

\*Corresponding author. qiaojl@dhu.edu.cn, keryn.lian@utoronto.ca

Tel: +86-21-67792379. Fax: +86-21-67792159.

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**Abstract.** This paper reports the preparation and electro-catalytic activity of MnO<sub>2</sub> nanotube catalysts for both oxygen reduction reaction (ORR) and oxygen evolution reduction (OER) in alkaline media. The catalysts were synthesized by a simple hydrothermal method under controlling the different temperatures. Results of electrochemical characterization with emphasis on the activity of the catalyst are presented, which was demonstrated by cyclic voltammetry (CV) and linear sweep voltammetry (LSV) employing a rotating disk electrode (RDE) technique. The experiments show that the as-prepared MnO<sub>2</sub> catalyst with nanotube structure exhibited high electro-catalytic activity and stability during battery discharge, charge and cycling processes in 6 M KOH electrolyte. The primary Zn-air battery showed a discharge peak power density  $\sim 293 \text{ mW cm}^{-2}$ , which corresponds to the energy density  $\sim 725 \text{ mA hg}^{-1}$ . The rechargeable Zn-air battery exhibited a small charge–discharge voltage polarization of  $\sim 0.7 \text{ V}$  at  $10 \text{ mA cm}^{-2}$ , high reversibility and stability over short charge and discharge cycles, and  $\sim 1.1 \text{ V}$  for a long charge and discharge cycles test.

## Introduction

With the rapid development of the world economy, the energy crisis and environmental problems have become increasingly prominent [1]. To overcome this challenge, strategies have to be proposed to make a transition from a fossil fuel based economy to a clean energy economy. Electrochemical devices such as fuel cells, batteries and super capacitors are most potential alternatives for energy conversion and storage instead of the burning of fossil fuels. Therefore, many efforts have been focused on batteries and fuel cells, which can be used for EVs propulsion and large-scale energy storage. Among the different energy storage systems, the rechargeable zinc-air battery evoked a great interest due to its many attractive features including high energy density, cost-effective and environmentally friendly design, as well as low operating risks [2]. The excellent properties of rechargeable zinc-air batteries lead to potential applications in areas, such as stationary and portable power applications including electric vehicles [3,4].

Zinc-air batteries have a high theoretical energy density of  $1086 \text{ Wh kg}^{-1}$  (including oxygen), about five times higher than the current lithium-ion technology [5]. They can be potentially manufactured at very low cost ( $<10 \text{ \$ kW}^{-1} \text{ h}^{-1}$  estimated, about two orders of magnitude lower than lithium-ion). For many applications, zinc-air batteries offer the highest available energy density of

any primary battery systems. However, in a rechargeable zinc-air battery, oxygen evolution reaction (OER) and oxygen reduction reaction (ORR) occur on the air electrode during battery charge and discharge process, respectively. The sluggish reaction kinetics and large over potential associated with OER and ORR greatly limit the performance of rechargeable zinc-air batteries [2,4]. To date, for most fuel cells, the most practical cathode catalysts are still Pt-based materials for improving the sluggish kinetics of oxygen reduction reaction. As yet, the high cost and the poor stability of Pt-based noble metal catalysts hinder this technology's commercialization. As a result, an affordable, active and stable bifunctional catalyst is an urgent issue for improving the performance of rechargeable zinc-air batteries. In this article, we reported the synthesis of MnO<sub>2</sub> nanotube catalysts, and their electro-catalytic activity for both ORR and OER including charge-discharge properties when used as air cathode electrode were studied.

## Experimental

**Catalyst preparation.** MnO<sub>2</sub> nanotube catalysts were prepared through a facile hydrothermal method. In a typical experiment, 0.7963 g KMnO<sub>4</sub> and 2 mL concentrated HCl (37%) were added to 50 mL deionized water to form the precursor solution, then the solution was transferred into a 100 mL teflon-lined stainless steel autoclave. The autoclave was sealed and hydrothermally treated at 100, 140, 180 and 220°C for 12 h. After the autoclave was cooled down to room temperature naturally, the MnO<sub>2</sub> nanotube sample was collected and washed 3-5 times with deionized water and ethanol. Then the products were dried in air at 75°C for 24 hours. After that, the resulting products were calcined in air at 350°C for 1 h.

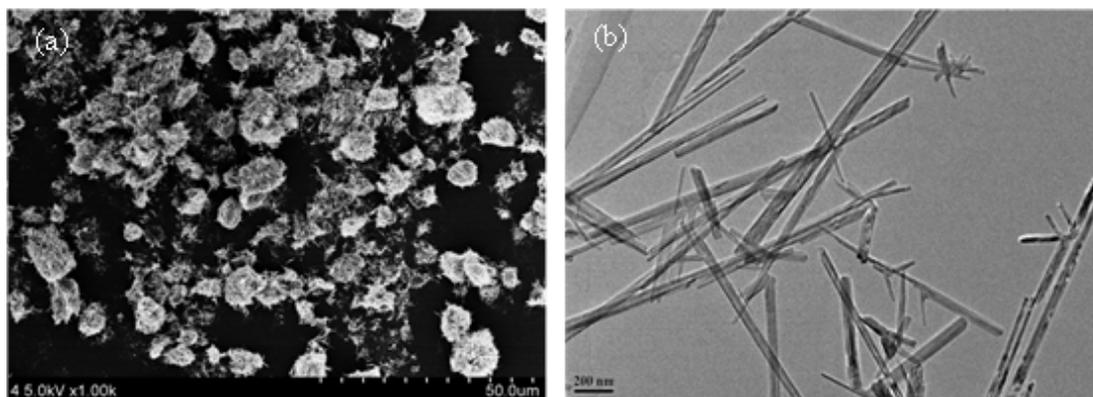
**Electrode preparation and electrochemical measurements.** In this experiment, we use a rotating disc electrode (RDE) half-cell setup to investigate the ORR and OER catalytic activity of the MnO<sub>2</sub> nanotube catalyst samples. The working electrode was fabricated by casting Nafion-impregnated catalyst ink onto a glassy carbon disk electrode (5.6 mm in diameter). 5 mg of the catalyst was ultrasonically dispersed into 1 mL ethanol and 8 μL 5 wt% Nafion solution to form a catalyst ink. After that, 8 μL of the catalyst ink was dropped onto disk electrode and dried naturally at room temperature. The working electrode was allowed to achieve a catalyst loading of 0.1 mg cm<sup>-2</sup>, which was then immersed in a glass cell containing 0.1 M KOH aqueous electrolyte during the whole measurements. Electrochemical activity of the MnO<sub>2</sub> nanotube catalyst samples were tested through linear sweep voltammetry. A Pt/C electrode was used as the reference electrode. Catalyst activity toward ORR and OER was evaluated in oxygen-saturated electrolyte solution from 1.67 to 0.1 V vs RHE. The potential of the reference electrode was normalized with respect to the potential of the reversible hydrogen electrode (RHE). The rotation rate is 1500 rpm and the scan rate is 5 mVs<sup>-1</sup>. A commercial Pt/C catalyst (30 wt%, JM) was tested using the same procedures.

**Materials Characterization.** The morphologies of various catalyst samples were evaluated using an FEI Sirion 200 field-emission scanning electron microscope (SEM) operating at 5 kV. And transmission electron microscopy (TEM) images were taken by a JEOL JEM 2010F microscope at an accelerating voltage of 200 kV.

**Zinc-air batteries measurements.** A home-made zinc-air battery was used to validate the practical catalyst activity and stability. The air cathode was prepared by spraying the catalyst (with a loading of 2 mg cm<sup>-2</sup>) onto a piece of carbon paper with an exposed active area of 4 cm<sup>2</sup>. Briefly, 30 mg of catalyst was dispersed in 10 mL of ethanol by sonication for 30 minutes. 80 μL of 5 wt% Nafion® solution was added followed by additional sonication for 1h. Then the catalyst mixture was sprayed onto the carbon paper and dried in an oven at 60°C for 1 hour. The catalyst loading was controlled by calculating the weight of the air electrode with the carbon paper before and after

the spray coating. 10 mL of 6 M KOH was used as the electrolyte in the zinc–air battery, and a polished zinc plate (purity > 99.99%, thickness: 1.0 mm, Shengshida Metal Mater. Co. Ltd, China) was used as the anode. A Galvano dynamic method with a current density ranging from 0 to 1000 mA were used to obtain the discharge polarization and power density plots. Battery testing and cycling experiments were performed under 25°C using the recurrent galvanic pulse method, where one cycle consisted of a discharging step (5 mA cm<sup>-2</sup> for 10 minutes) was conducted followed by a charging step of the same current and duration time.

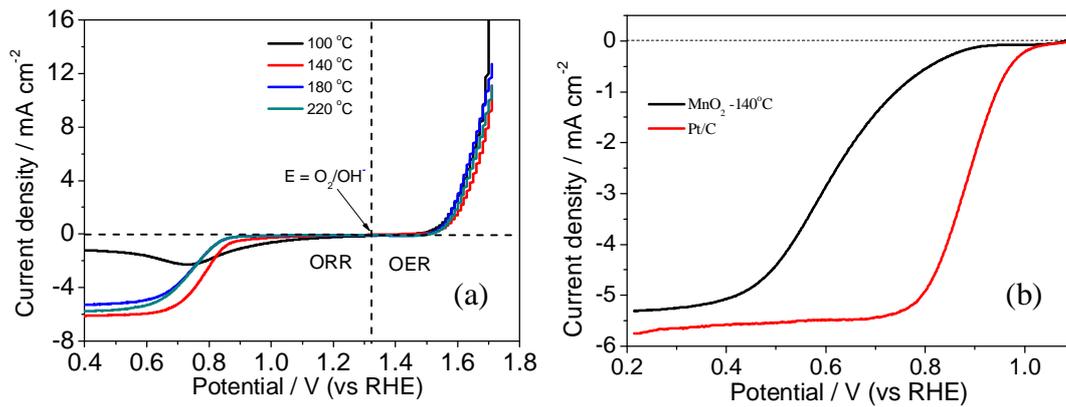
## Results and Discussion



**Fig. 1** (a) SEM image of MnO<sub>2</sub>; (b) TEM image of MnO<sub>2</sub>.

**Surface Structure of MnO<sub>2</sub> nanotube catalyst.** In fig. 1(a-b), SEM and TEM images are provided, where the morphologies of the catalyst sample was examined. Fig. 1(a) reveals the typical SEM image of the MnO<sub>2</sub> nanomaterials. It can be seen that MnO<sub>2</sub> nanotubes can be successfully synthesized by applying the simple one-step hydrothermal method. Moreover, this SEM image demonstrated that MnO<sub>2</sub> nanotubes have clear texture structure on its surface under hydrothermal temperature of 140°C. Such texture structure made up of countless porous with the diameter between 0.43~0.45 nm. As shown in Fig. 1(b), MnO<sub>2</sub> nanotubes consisting of average diameter and length of 12 nm and 45~60 nm, respectively, can be clearly observed. More importantly, the mechanical strength will be increased and the surface area will increase due to the small the particle size, which will directly improve the stability and activity of the catalyst.

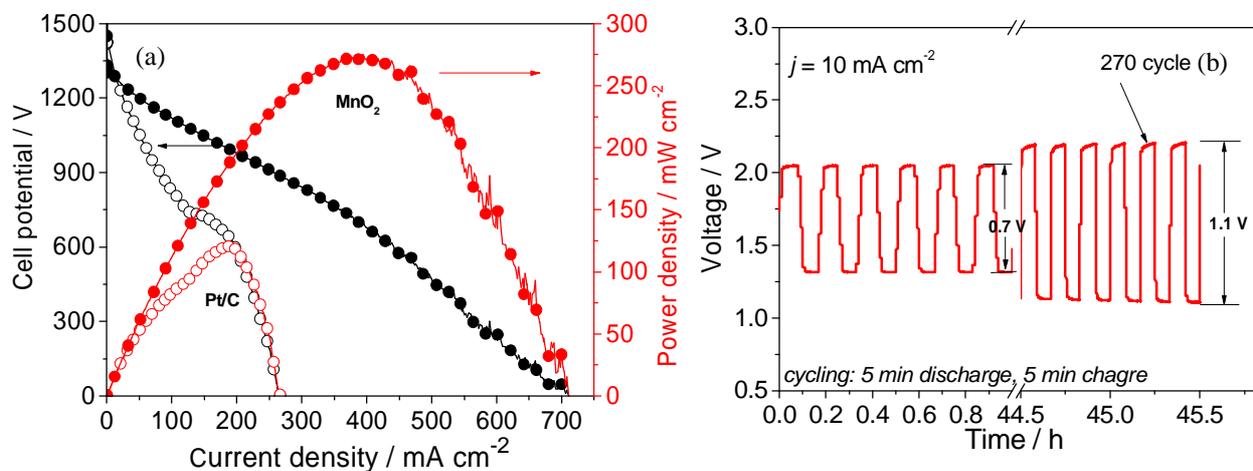
**Linear sweep voltammetry.** For further investigating the electro-catalytic activity for both ORR and OER, LSV study was conducted in O<sub>2</sub> saturated 0.1 M KOH solution using a rotating disk electrode. Fig. 2(a) shows the LSV curves at different hydrothermal temperatures for MnO<sub>2</sub> nanotube catalyst. It can be seen that hydrothermal temperature has great effect on MnO<sub>2</sub> catalysts' performances. As shown in Fig. 2 (a), the onset potential for ORR was detected at 0.94 V for MnO<sub>2</sub> nanotube catalyst synthesized at 140°C, whereas the onset potentials of 0.91 V, 0.79 V and 0.78 V were observed for MnO<sub>2</sub> nanotubes synthesized at 100, 180 and 220°C, respectively. At 0.4 V, the MnO<sub>2</sub> nanotube catalyst synthesized at 100, 140, 180 and 220°C afforded an ORR current density of 1.2 mA cm<sup>-2</sup>, 6.1 mA cm<sup>-2</sup>, 5.2 mA cm<sup>-2</sup> and 5.8 mA cm<sup>-2</sup>, respectively. Apart from the ORR activity, good OER activity is particularly critical for MnO<sub>2</sub> bi-functional catalysts. From Fig. 2(a), it can be seen that the onset potential was detected at 1.45 V for MnO<sub>2</sub> nanotube catalyst synthesized at 140°C, whereas it was 1.51 V, 1.56 V and 1.53 V for MnO<sub>2</sub> nanotube catalyst synthesized 100, 180 and 220°C, respectively. The OER current densities for MnO<sub>2</sub> nanotube catalyst synthesized 100, 140, 180 and 220°C at 1.7 V are 16, 9, 12 and 14 mA cm<sup>-2</sup>, respectively.



**Fig. 2** (a) ORR and OER polarization curves of  $\text{MnO}_2$  by 100, 140, 180 and 220°C;

In addition, the  $\text{MnO}_2$  nanotubes catalyst synthesized at 140°C can give a much high catalytic ORR current density of  $6.1 \text{ mA cm}^{-2}$  accompanied by a defined diffusion-limiting current plateau at 0.4 V, which is almost 1.5 times of Pt/C catalyst (Fig. 2(b)).

**Primary Zn-air batteries.** To practically confirm that the  $\text{MnO}_2$  materials could be used as electro-catalysts for Zn-air battery, here the  $\text{MnO}_2$ -140 catalyst as-synthesised was used as the ORR catalyst loaded on the carbon fibre paper as cathode. With the cathode prepared, we install it with a Zn foil (0.5 mm thickness) as anode and 6 M KOH as the electrolyte to make up a primary Zn-air battery. As shown in Fig. 3(a), the primary battery showed a high open circuit voltage of  $\sim 1.325 \text{ V}$ . At a voltage of 1.0 V, it gave a high current density of  $200.6 \text{ mA cm}^{-2}$ . The peak power density could reach as high as  $293.2 \text{ mW cm}^{-2}$  at 0.7 V, much better than that of most recently reported Zn-air primary battery [6]. In addition, our catalyst has much higher peak power density compared with Pt/C ( $120.8 \text{ mW cm}^{-2}$ ) under the same measuring conditions. Recently, Zn-air fuel cells or Zn-air flow batteries have been proposed and demonstrated to power electric vehicles with high power, long driving distance and commercial viability [7]. The above results indicate that the nanotube catalyst developed in this work should be ideally suited for such traditional primary Zn-air batteries owing to the decent high ORR activity and durability.



**Fig. 3** (a) Polarization curve and corresponding power density plots of the primary Zn-air battery using the  $\text{MnO}_2$  catalyst; (b) Charge and discharge polarization (V-i) curves of the rechargeable Zn-air battery.

**Rechargeable Zn-air batteries.** For further demonstrating MnO<sub>2</sub> nanotube catalyst developed above in practical application, an electrochemically rechargeable Zn-air batteries was constructed and tested by utilizing the as-prepared MnO<sub>2</sub> nanotube materials as the cathode catalyst. Fig. 3(b) shows the charge and discharge polarization curves of the rechargeable Zn-air battery. As can be seen clearly from the Fig. 3(b), our rechargeable Zn-air battery exhibits a remarkable stable cycling stability with a narrow charge-discharge voltage gap of 0.7 V, and the discharge voltage can be able to maintain above 1.3 V. This suggests that the homemade Zn-air battery exhibits a stable cycling stability when it was charged and discharged at controlled current densities (10 mA cm<sup>-2</sup>) and cycling pattern (5 minute per charge or discharge period). Even after 44 hours, our rechargeable Zn-air battery can still show a narrow charge-discharge voltage gap (~1.1 V), indicating the long term durability of the catalyst. Considering that the battery oxidant feeding was by an un-enforced atmosphere air instead of pure oxygen or enforced air flow, the results described above are significantly improved.

## Conclusions

In summary, the MnO<sub>2</sub> nanotubes as a new kind of air electrode catalyst have been synthesized via a simple one-step hydrothermal method. Particularly, the MnO<sub>2</sub> nanomaterial was used as a highly active bi-functional cathode catalyst for rechargeable Zn-air battery. The maximum power density can achieve as high as 272.9 mW cm<sup>-2</sup>, and a high current density 183.9 mA cm<sup>-2</sup> at 1.0 V. Moreover, the rechargeable battery shows the high performance with an excellent cycling stability. All of these battery tests have confirmed that the MnO<sub>2</sub> bi-functional catalyst developed in this work is feasible and promising for practical application of Zn-air batteries.

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## References

- [1] S.I. Smedley and X.G. Zhang: *J. Power Sources* Vol. 165 (2007), p. 897-904.
- [2] V. Neburchilov, H.J. Wang, J.J. Martin and W. Qu: *J. Power Sources* Vol. 195 (2010), p. 1271-1291.
- [3] J. Goldstein, I. Brown and B. Koretz: *J. Power Sources* Vol. 80 (1999), p. 171-179.
- [4] P. Sapkota and H. Kim: *J. Ind. Eng. Chem.* Vol. 15 (2009), p. 445-450.
- [5] Y.G. Li, H.J. Dai: *Chem. Soc. Rev.* Vol. 43 (2014), p. 5257-5275.
- [6] G.J. Du, X.D. Liu, Y. Zong, T.S. Hor, A.Y. Yu and Z.L. Liu: *Nanoscale* Vol. 5 (2013), p. 4657-4661.
- [7] J. Hu, L. Wang, L.N. Shi and H. Huang: *J. Power Sources* Vol. 269 (2014), p. 144-151.