Electronic Supplementary Information (ESI)

ε-MnO_2 Nanostructures Directly Grown on Ni foam: A Cathode Catalyst for Rechargeable Li-O_2 Batteries

Xiaofei Hu, Xiaopeng Han, Yuxiang Hu, Fangyi Cheng* and Jun Chen*

Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China; Collaborative Innovation Center of Chemical Science and Engineering, Tianjin 300071, China. Fax: 86-22-23509571, Tel: 86-22-23504482

(F. Cheng) E-mail: fycheng@nankai.edu.cn; (J. Chen) E-mail: chenabc@nankai.edu.cn

Materials Synthesis

Nanostructured ε-MnO_2 was prepared by electrodeposition on Ni substrate. All electrodeposition experiments were carried out in a three-electrode system. A saturated calomel electrode in saturated KCl solution was used as the reference electrode and a platinum foil was used as the counter electrode. Nanostructured ε-MnO_2 was deposited onto Ni foams by applying a current density of 5.0 mA cm^{-2} in a solution bath containing 0.1 M manganous acetate and 0.1 M sodium sulfate for 5 min at 35 °C.[1, 2, 3] Prior to the electrodeposition, the Ni foam was washed with acetone and distilled water and dried at 120 °C in a vacuum oven for 6 h. The plating solution was stirred continuously by a Teflon stir on a hot plate during the deposition. After deposition, the plated foils were rinsed several times in distilled water and dried in air. The electrodeposited electrodes were annealed in air at varied temperatures for different time: 150 °C/350 °C/ 450 °C/550 °C/650 °C for 15 h, and 350 °C for 15 h/60 h/80 h.

Cell Assembly

The CR2032-type cell assembly was conducted in an Ar-filled glovebox by stacking a newly polished lithium metal foil anode (1.54 cm^2), a glass fiber separator (nominal thickness 0.30 mm, porosity 92%-98%, purchased from Beijing ShengHeChengXin membrane technology development center) soaked by three drops of electrolyte and an ε-

MnO_2/Ni cathode (geometric area, 0.78 cm^2) placed in a cell case. The positive top cover was machine-drilled to create 13 evenly distributed 1.5 mm-diameter holes to enable oxygen flow. The electrolyte was 1 M lithium bis(trifluoromethylsulfonyl)amide (LTFSI) in tetra(ethylene glycol)-dimethyl-ether (TEGDME). After assembly, the cell was transferred to a sealed glass box filled with 1 atm high-purity oxygen.

Materials Characterization

X-ray diffraction (XRD, Rigaku MiniFlex600, Cu Kα radiation) was used to identify the product and the scanning speed was 4° min^{-1}. The microstructures and morphologies were characterized by high resolution transmission electron microscopy (HRTEM, tecnai G2 F20) and scanning electron microscopy (SEM, JEOL, JSM–7500F). The specific surface area and pore size distribution (BET) were analyzed by nitrogen adsorption–desorption measurement (BEL JAPAN, INC., BELSORP–Mini) at 77 K. Thermogravimetric (TG) analysis was performed on Netzsch, STA 449 F3. The amount of deposited MnO_x was measured by weighing the nickel foam substrate before and after electrodeposition using the high-resolution balance in TG analyzer. The mass ratio of MnO_2 to Ni is near 1%. The composition of MnO_x samples was determined by chemical titration.[4] Procedures of chemical titration: (1) Samples (mass: m_1) were dissolved in mixed solution of dilute sulphuric acid (10 mL) and standard solution of sodium oxalate (volume: $V_{Na2C2O4}$; concentration: $C_{Na2C2O4}$). Then, the resultant solution was back titrated by $KMnO_4$ (volume: V_{KMnO4}; concentration: C_{KMnO4}). (2) Samples (mass: m_2) were dissolved in concentrated hydrochloric acid (2 mL), which was diluted by distilled water (50 mL). Then, ascorbic acid (~0.1 g) and eriochrome black t were added. The resultant solution was titrated by EDTA (Ethylene Diamine Tetraacetic Acid, volume: V_{EDTA}; concentration: C_{EDTA}). Manganese valence state = $[2 \times (C_{Na2C2O4}V_{Na2C2O4} - 2.5 \times C_{KMnO4}V_{KMnO4})/m_1]/[C_{EDTA}V_{EDTA}/m_2]$.

Electrochemical Measurements

After being kept in oxygen atmosphere for 8 h at the open-circuit state (voltage is ~3.3 V vs. Li/Li$^+$), the assembled batteries were cycled at different charge/discharge current densities in the voltage range of 2.2–4.3 V on a CT2001A cell test instrument (LAND Electronic Co.). The specific capacity was calculated on the basis of the amount of ε-MnO_2. The amount of manganese oxide as a cathode material in a Li–O_2 cell was about 0.4 mg cm^{-2}. The cyclic voltammograms (CV) were performed at 0.1 mV s^{-1} with a Parstat 263A electrochemical workstation (AMTECT Company). The electrochemical impedance spectroscopy (EIS) was conducted using Parstat 2273 potentiostat/galvanostat workstation (AMETEK) within the frequency range of 100 kHz–10 mHz at room temperature.

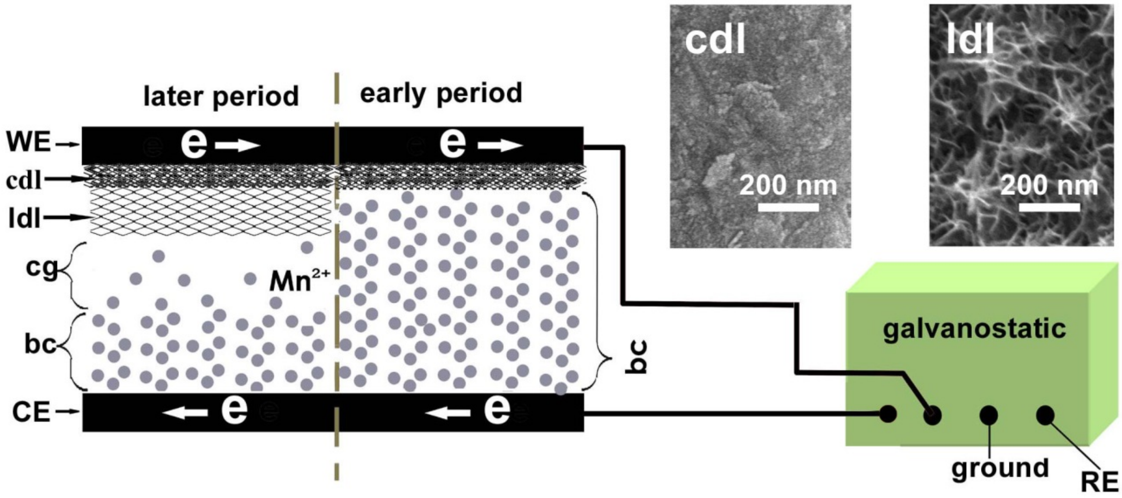

Fig. S1 Schematic illustration of the synthesis of interconnected ε-MnO_2 nanostructures on Ni foam at 35 °C. WE: work electrode (Ni foam); CE: counter electrode (Pt foil); cdl: compact deposition layer; ldl: loose deposition layer; cg: concentration gradient; bc: body concentration; RE: reference electrode (saturated calomel electrode in saturated KCl solution). The RE was placed next to work electrode and counter electrode in the electrolyte. To simplify the illustration, only WE and CE are shown in the left part of the scheme. SEM mages of cdl and ldl are shown for comparison. The formation of cdi and ldl is possibly ascribed to the following points. At the early period of electrodeposition, nucleation and crystal growth occur evenly on the substrate, favouring the formation of compact layer. As electrodeposition proceeds, the Mn^{2+} concentration of bath solution decreases and further crystal growth tends to unevenly participate at preferred sites, resulting in loose layer.

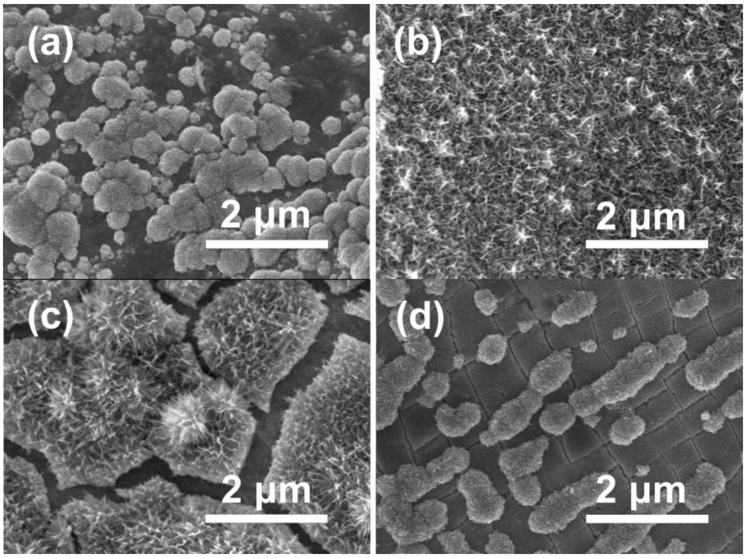

Fig. S2 SEM images of ε-MnO_2 prepared by electrodeposition at (a) 0 °C, (b) 25 °C, (c) 45 °C, and (d) 60 °C. It is noted that the samples synthesized at 25 °C show similar morphology to that obtained at 35 °C.

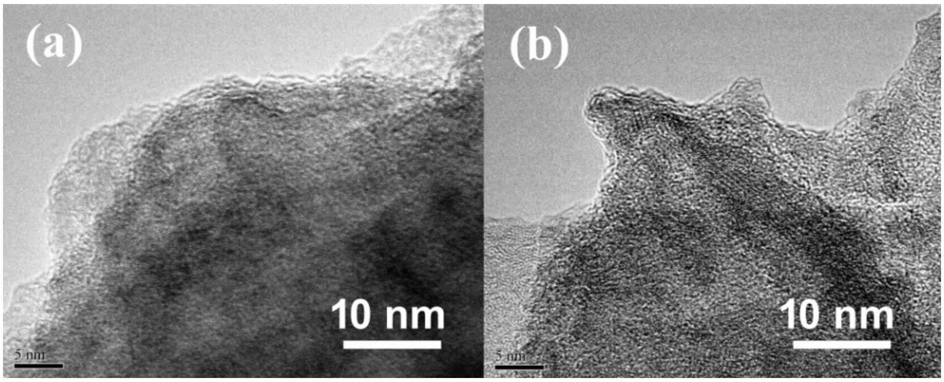

Fig. S3 HRTEM images of ε-MnO_2 electrodes treated at (a) 35 °C and (b) 150 °C for 15 h.

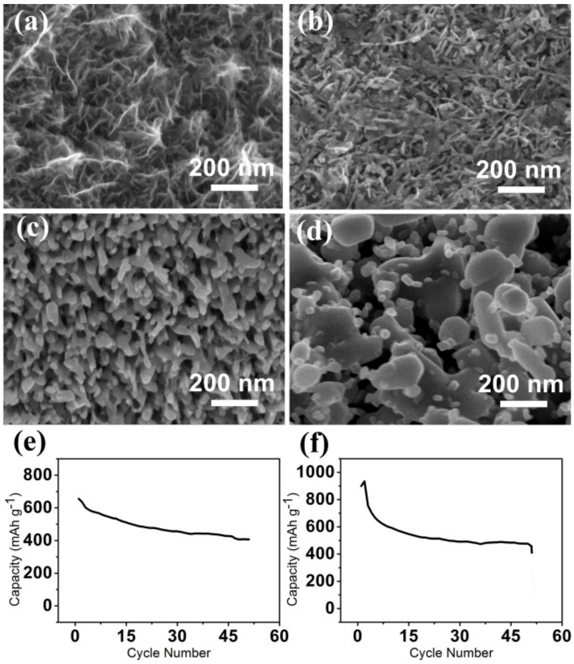

Fig. S4 SEM images of ε-MnO_2 treated at (a) 150 °C, (b) 450 °C, (c) 550 °C and (d) 650 °C for 15 h. The cycling performance of (e) 15 h@150 °C and (f) 15 h@450 °C electrodes at a current of 800 mA g^{-1}.

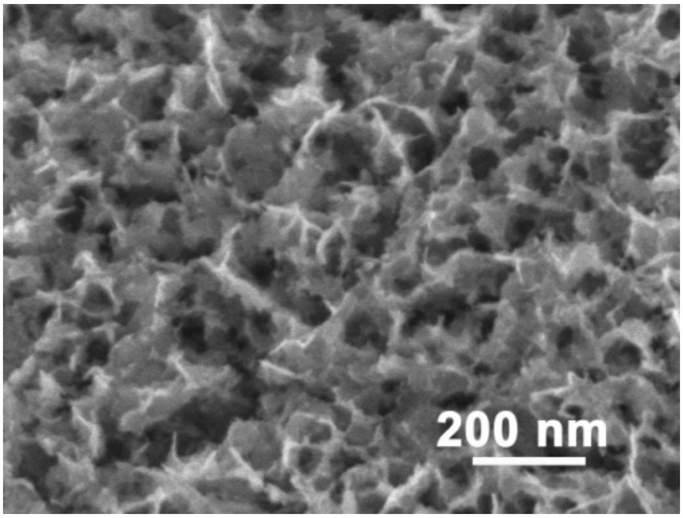

Fig. S5 SEM image of ε-MnO_2 electrode treated at 350 °C for 80 h.

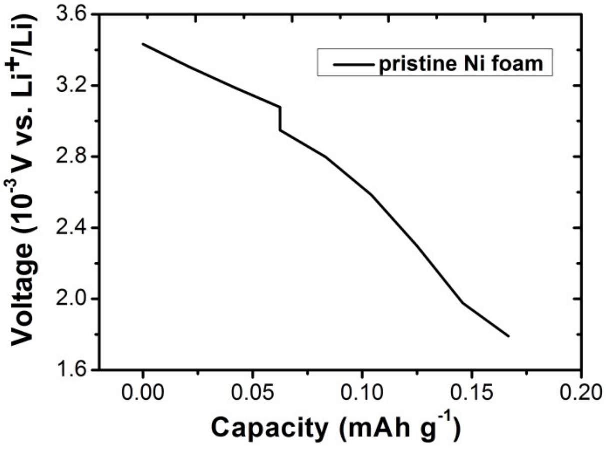

Fig. S6 The first discharge profile of pristine Ni foam as a cathode material in a Li–O_2 cell. Apparently, pristine Ni foam itself contributes negligible to the capacity of the cathode.

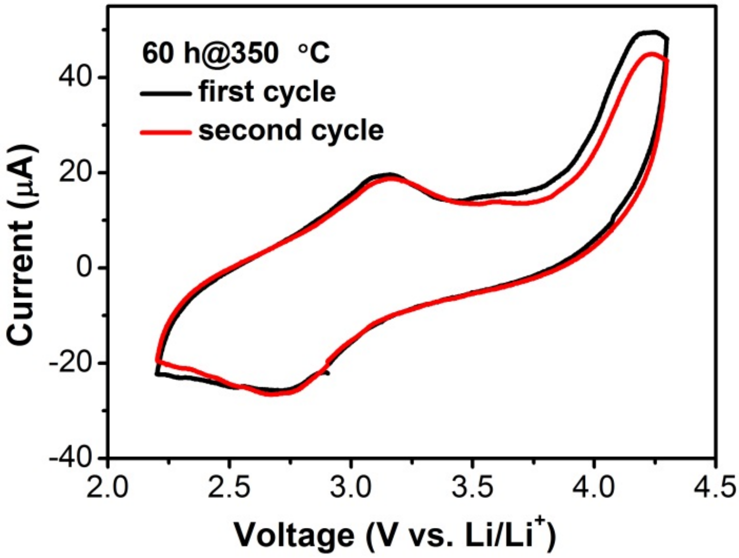

Fig. S7 CV profiles of ε-MnO_2 nanostructures treated at 350 °C for 60 h. Sweep speed is 0.1 mV s^{-1}.

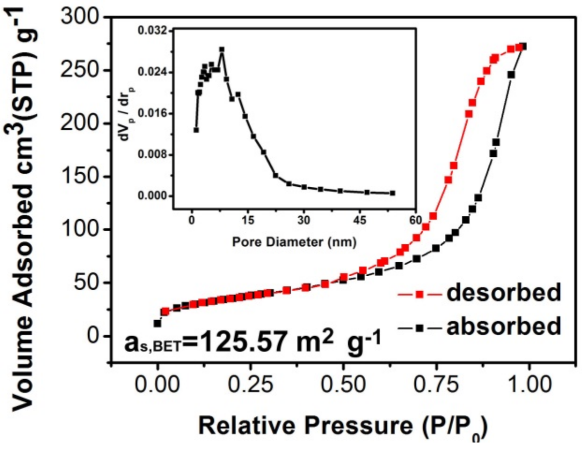

Fig. S8 N_2 adsorption-desorption isothermal and pore-size distribution curves (inset) of ε-MnO_2 (scraped off the Ni substrate) annealed at 350 °C for 60 h.

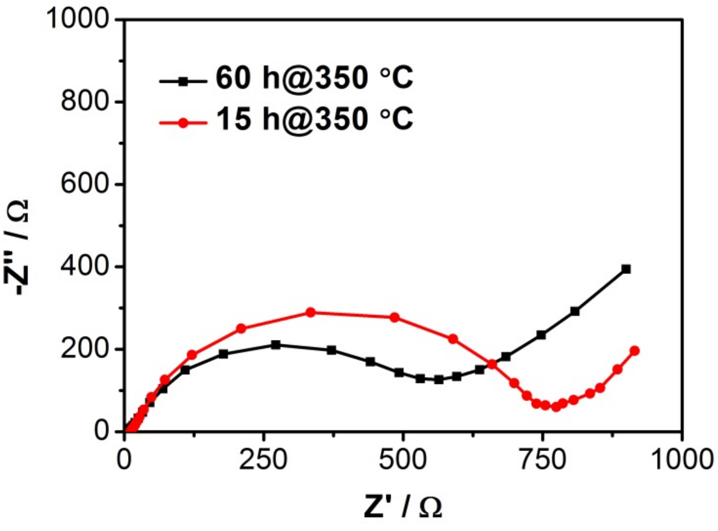

Fig. S9 Electrochemical Impedance Spectroscopy (EIS) recorded before discharge for cells assembled with electrodes of 60 h@350 °C and 15 h@350 °C ε-MnO_2/Ni samples.

Table S1 Comparison of the electrochemical performance of MnO_2-based electrodes reported in literatures and the present study.

Sample	Voltage range / V	Cycling performance / cycle	Capacity / mAh g^{-1}
α-MnO_2 nanowires[5]	2.00−4.15	10	3000−1600
α-MnO_2 needles[6]	2.20−4.30	20	2300−800
reduced graphene oxide/α-MnO_2 nanorod composite[7]	2.00−4.80	8	570−100
α-MnO_2 nanorods[8]	2.20−4.30	60	500
our samples	2.20−4.30	>120	> 1000

Supplementary References

1. M. S. Wu, P. C. J. Chiang, J. T. Lee and J. C. Lin, *J. Phys. Chem. B*, 2005, **109**, 23279.

2. D. Tench, L. F. Warren, *J. Electrochem. Soc.*, 1983, **130**, 869.

3. S. L. Chou, F. Y. Cheng, J. Chen, *J. Power Sources*, 2006, **162**, 727.

4. F. Y. Cheng, T. R. Zhang, Y. Zhang, J. Du, X. P. Han and J. Chen， *Angew. Chem. Int. Ed.*, 2013, **52**, 2474.

5. A. Debart, A. J. Paterson, J. L. Bao, and P. G. Bruce, *Angew. Chem. Int. Ed.*, 2008, **47**, 4521.

6. L. Trahey, N. K. Karan, M. K. Y. Chan, J. Lu, Y. Ren, J. Greeley, M. Balasubramanian, A. K. Burrell, *Adv. Energy Mater.*, 2013, **3**, 75.

7. Y. Yang, B. Zhang, Y. B. He, Z. D. Huang, S. W. Oh and J. K. Kim, *J. Mater. Chem. A*, 2013, **1**, 1163.

8. Y. Qin, J. Lu, P. Du, Z. H. Chen, Y. Ren, T. P. Wu, J. T. Miller, J. G. Wen, D. J. Miller, Z. C. Zhang and K. Amine, *Energy Environ. Sci.*, 2013, **6**, 519.