Supplementary Information

Manganese oxide/carbon composite nanofibers: electrospining preparation and application as a bi-functional cathode for rechargeable lithium-oxygen batteries

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Materials preparation and characterizations

Mn_3O_4/C nanofibers were prepared by the electrospinning technique as follows: 3.5 g of polyacrylonitrile (PAN) and 1.5 g of manganese acetate ($Mn(OAc)_2$) were dissolved in 45 g of N,N-dimethylformamide (DMF) and, then, the mixture was continuously stirred at room temperature to form a homogeneous solution for 48 h. The solution was ejected through the needle tip under a strong electric field (15 kV), and the PAN/$Mn(OAc)_2$ fibers were accumulated on the collection drum and collected as a fibrous mat. The electrospun fibers were heat-treated in an Ar atmosphere at 280^{o}C for 5 h and, then, in a mixture of Ar and air at 500^{o}C for 2 h. The flow rate was 1 L min^{-1}.

The phase analysis of the synthesized nanofibers was performed with an automated HPC-2500 XRD diffractometer (Gogaku) using Cu K_α radiation (λ = 1.5405 Å). The XRD measurements were conducted over the scanning angle range of 10 – 90^o at a scan rate of 5^o min^{-1} using a step width of 0.02^o. The thermogravimetric analysis (TGA/SDTA851e-METTLER) was performed in a temperature range of 25 – 550^{o}C with a heating rate of 2^{o}C min^{-1} in air. The morphology and microstructure were examined with the scanning electron microscopy (SEM, Hitachi S4700) and the transmission electron microscopy (TEM, TECNAI G2 F30S-Twin) in conjunction with energy dispersive spectroscopy (EDS). The Brunauer-Emmett-Teller (BET) surface area and the total pore volume were measured by using a BEL-SORP mini system.

Electrochemical experiments

(a) Rotating-disk electrode (RDE) experiments

RDE experiments were performed in a three-electrode electrochemical cell using a potentiostat (CH Instrument) at room temperature. An RDE with a glassy carbon substrate was used as the working electrode. The catalyst and the conductive carbon (Ketjen Black, KB) were mixed and, then, the ink was prepared by dispersing the mixture in distilled water in an ultrasonic bath. The electrode compositions are as follows:

(1) KB: 100 wt.% KB

(2) Mn_3O_4 + KB: 50 wt.% Mn_3O_4 powder + 50 wt.% KB

(3) Mn_3O_4/C nanofiber + KB: 50 wt.% Mn_3O_4/C nanofiber + 50 wt.% KB

The suspension (20 μL) was deposited onto the glassy carbon electrode that had been polished with Al_2O_3 powders. After drying, 5 μL of Nafion solution (5 wt.%) was coated onto the catalyst layer. The Nafion coating is widely used in RDE experiments to ensures the better adhesion of the catalyst layer on the glassy carbon substrate without disturbing the electrochemical signal.[1,2] The electrolyte was 0.1 M KOH solution. A platinum wire and an Ag/AgCl electrode were used as the counter and reference electrodes, respectively. All potentials in this work were referred to a reversible hydrogen electrode (RHE). The oxygen gas was purged throughout the RDE experiments to make the electrolyte saturated with oxygen, and the linear sweep voltammogram was recorded at a rate of 10 mV s^{-1} by scanning the electrode potential between 1.1 and 0.4 V *vs.* RHE for ORR and between 1.0 and 2.0 V *vs.* RHE for OER.

(b) Evaluation of hybrid Li-O_2 battery performances

To prepare the cathode for electrochemical testing in a Li-O_2 battery, a composite powder of the catalyst and the conductive carbon was mixed with poly(tetrafluoroethylene) (PTFE) binder in ethanol. The electrode compositions are as follows:

(1) KB: 95 wt.% KB + 5 wt.% PTFE

(2) Mn_3O_4 + KB: 30 wt.% Mn_3O_4 powder + 65 wt.% KB + 5 wt.% PTFE

(3) Mn_3O_4/C nanofiber + KB: 30 wt.% Mn_3O_4/C nanofiber + 65 wt.% KB + 5 wt.% PTFE

Then, the mixture was pressed with a twin roller and dried under vacuum at 60°C for 24 h. Finally, the cathode was prepared by pressing the composite sheet (thickness = *ca.* 200 μm) onto a nickel mesh current collector. The electrode loading was 30 mg cm^{-2}.

The Li-O_2 cell with a hybrid electrolyte consists of a lithium foil anode, a non-aqueous electrolyte, an LTAP solid membrane, an aqueous electrolyte, and a cathode. Fig. S1 illustrates the schematic diagram of the hybrid Li-O_2 cell. The anode compartment was assembled by stacking (*i*) a copper mesh current collector, (*ii*) a lithium foil, (*iii*) a separator (Celgard 2450) impregnated with 1 M LiTFSI in TEGDME, and (*iv*) an LTAP solid membrane (OHARA Inc.). It was sealed using an Al pouch, leaving a square window of 2.5 × 2.5 cm^2. The anode was fabricated in a glove box filled with purified Ar gas. After the sealed anode was taken out of the glove box, an aqueous electrolyte (1 M $LiNO_3$ + 0.5 M LiOH) was poured on the top of the LTAP solid membrane and, then, the cathode was placed on the aqueous electrolyte. O_2 gas was

supplied to the cathode compartment through a tube. The electrochemical performance of the Li-O_2 battery was evaluated by a galvanostatic charge-discharge method with a Maccor series 4000.

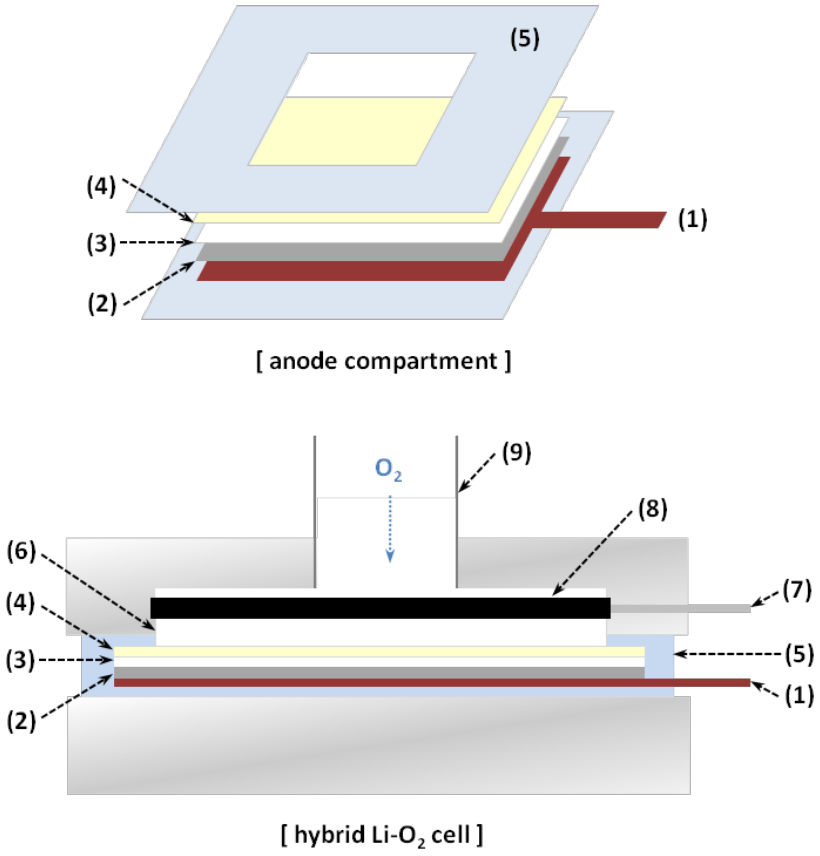

Fig. S1 Schematic diagram of the hybrid Li-O_2 cell used for electrochemical tests.

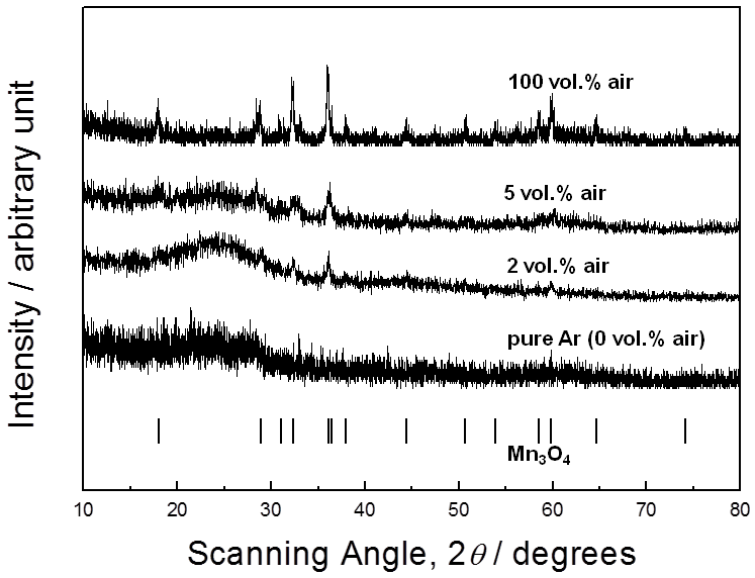

Fig. S2 XRD patterns of the electrospun PAN/$Mn(OAc)_2$ fibers heat-treated at 500°C in various atmospheres.

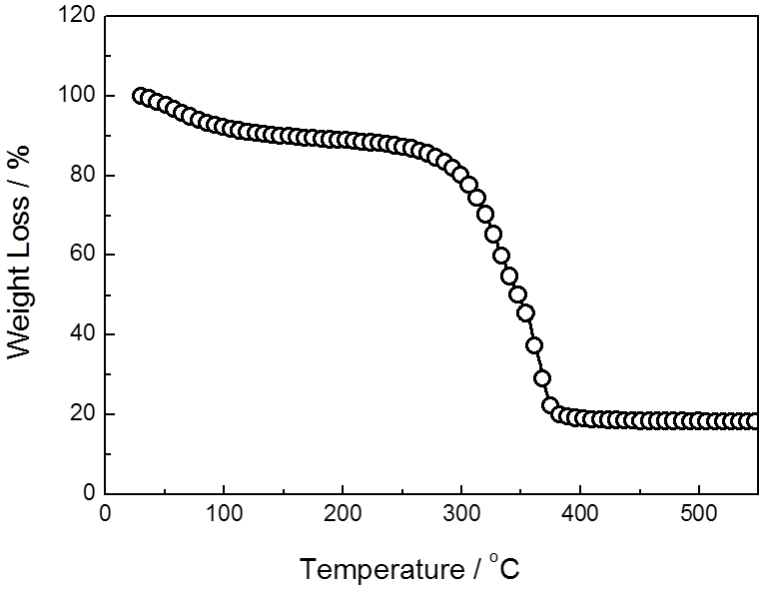

Fig. S3 TGA curve of the electrospun PAN/$Mn(OAc)_2$ fibers heat-treated in pure Ar at 500°C. The curve was measured in air during heating from room temperature to 550°C.

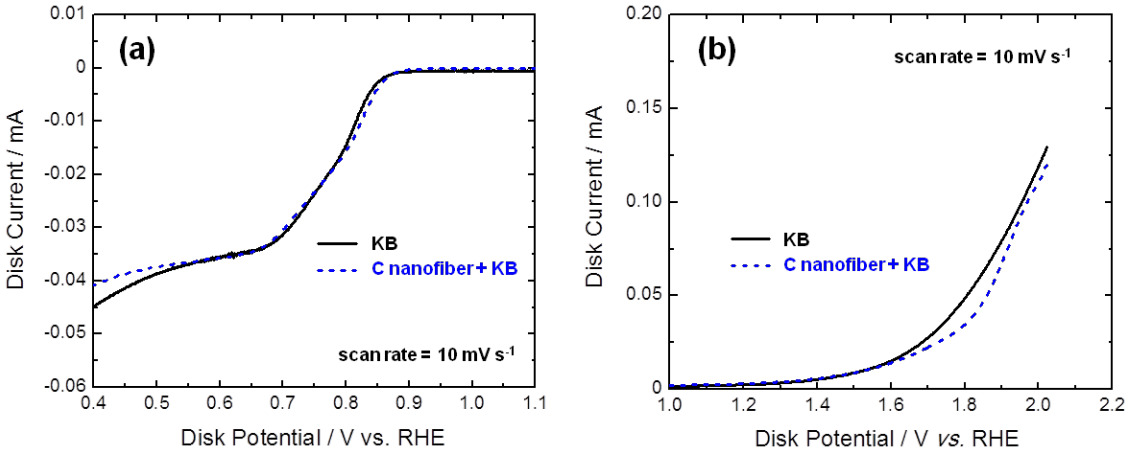

Fig. S4 (a) ORR and (b) OER polarization curves on the RDE at 1200 rpm in 0.1 M KOH for [KB] and [C nanofiber + KB].

References

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2. L. Wang, X. Zhao, Y. Lu, M. Xu, D. Zhang, R. S. Ruoff, K. J. Stevenson and J. B. Goodenough, *J.Electrochem. Soc.*, 2011, **158**, A1379.