A lithium-ion oxygen battery with lithiated Si anode by a Li₃N-containing cathode

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Experimental section

Materials

Lithium bis (trifluoromethane sulfonimide) (LiTFSI), fluroethylene carbonate (FEC), tetraethylene glycol dimethyl ether (TEGDME) were purchased from Do-Fluoride New Energy Technology. Li₃N was purchased from Alfa Aesar. In order to reduce the particle size, the Li₃N was ball-milled in Ar filled jar with 400 rpm for 2 hours. Silicon powder (crystalline, 30~50 nm) was obtained from HAOXI Research Nanomaterials, Inc. Polyacrylic acid (PAA) was obtained from Aladdin Reagent. Li₃N, super P and CNT were mixed by ball-milling to get a homogeneous mixture with mass ratio of 90:5:5.

Preparation of electrodes

Silicon powder, super P and PAA (weight ratio 75:15:15) were mixed together using water as solvent to obtain slurry. Then, the slurry was coated onto a copper foil and transfer to a vacuum oven to remove the H₂O at 60 °C for 10 hours. Finally, the coated foil was cut into pieces (diameter 12 mm) with Si mass loading of about 0.8 mg cm⁻². For the high Si loading (~3 mg cm⁻²), the slurry was coated onto a porous copper foam (diameter 12 mm). The oxygen cathodes were prepared by the following procedure: multi-wall CNT and poly(vinylidene fluoride) (PVDF) (weight ratio 8:2) were dispersed in the 1-methyl-2-pyrrolidone (NMP) solvent, then the slurry was coated onto carbon paper (diameter 12 mm), finally, the electrodes were dried in the vacuum oven at 100° C for 10 hours. The loading of CNT is ~0.4 mg cm⁻². The Li₃N loaded oxygen cathode was prepared by adding PTFE powder (10% wt) to the mixture of Li₃N, super P and CNT, and then it was pressed onto porous nickel foam (diameter 12 mm) at 10 Mpa, the Li₃N loading was ~8 mg per electrode.

Cell assembling and electrochemical measurement

The evaluation of Si electrodes was performed using CR2016 type coin cells with Si electrode (~0.8 mg cm⁻²), lithium metal, Polyethylene (PE) separator and different electrolytes (1 M LiPF₆ in EC-DMC-FEC (45:45:10 ν/ν), 1 M LiTFSI in TEGDME, 1M LiTFSI in TEGDME-FEC (98:2 ν/ν)). The cells assembled in glove box (H₂O and O₂ \leq 0.1 ppm) were tested on a LAND battery test system (CT2001A, Wuhan LAND electronics Co., Ltd., China) at 0.1 C (1 C=4000 mA g⁻¹s_i)

from 0.01 V to 1.2 V. The Li-O₂ battery was tested by assembling lithium metal, air cathode and electrolyte (1 M LiTFSI in TEGDME) in modified CR2032 type coin cells with several holes on the positive side. The assembled Li-O₂ cells were transferred into a glove box filled with pure O₂, then cycled at 250 mA g⁻¹ with fixed capacity of 500 or 1000 mAh g⁻¹ _{CNT}. For the Li || Li₃N cells, the Li₃N loaded air cathode, lithium metal, glass fiber separator and 1 M LiTFSI in TEGDME-FEC (98:2 ν/ν) electrolyte were assembled in the modified CR2032 type coin cell. The Si || Li₃N full cells were assembled like Li-O₂ cells by substituting CNT air cathode with Li₃N loaded air cathode, and its electrolyte was 1 M LiTFSI in TEGDME-FEC (98:2 ν/ν). The assembled Li || Li₃N half cells and Si || Li₃N full cells were transferred into the O₂ filled glove box, and then firstly charged to 3.6 V with current density of 100 mA g⁻¹ _{Si}. Afterwards, the Si || Li₃N cells were cycled at 200 mA g⁻¹ or 250 mA g⁻¹ with fixed capacity of 800 or 500 mAh g⁻² (based on the mass of carbon (CNT and Super P)). The amount of electrolyte used in these cells was ~50 uL.

Materials characterization

The Li₃N contained cathode, charged Li₃N contained cathode, Si anode and lithiated Si anode were characterized by field emission scanning electron microscopy (SEM, Nova NanoSEM 230, FEI company, USA), powder X-ray diffraction (XRD, D8 Advance, Bruker Corp., Germany) with Cu-K α radiation (λ =0.15418 nm) at 40 kV. The cycled lithium metal, cycled Si anode and discharged oxygen cathode were also characterized by SEM. The Li₃N, lithium metal, lithiated Si and Li₂O₂ are sensitive to the moisture and must be avoided to expose to atmosphere during the characterization process. The XRD samples were sealed with polyimide tape. The electrochemical impedance spectroscopy (EIS) was measured on an Autolab workstation (PGSTAT302N, Metrohm) in the frequency range from 100 KHz to 0.1 Hz. The cycled Li || Si half cells (1 cycle and 2 cycles) with 1 M LiTFSI in TEGDME-FEC (98:2 v/v) were disassembled and washed with 1 mL TEGDME, then the supernate was characterized by nuclear magnetic resonance (NMR). In situ gas chromatography-mass spectrometry (GC-MS) measurements were conducted using a homemade cell which was connected to the equipment (Clarus 680 and SQ 8S).



Fig. S1. The ¹⁹F NMR spectrum of the LTF-FEC and cycled LTF-FEC electrolytes. (Red: fresh 1 M LiTFSI in TEGDME-FEC (98:2 v/v), Green: 1 M LiTFSI in TEGDME-FEC (98:2 v/v) after 1 cycle, Black: 1 M LiTFSI in TEGDME-FEC (98:2 v/v) after 2 cycles)



Fig. S2. The result of in-situ GC-MS measurement of Li $\|$ Li₃N cell.



Fig. S3. (a) XPS spectrum of lithiated Si anode by Li₃N decomposition in the cathode, (b) Charge curve of Li || Li_xSi half cell.



Fig. S4. SEM images of discharged (a) and charged (b) oxygen cathodes of Li_xSi-O₂ cells.



Fig. S5. The charge and discharge curves of $Li-O_2$ (a) or Li_xSi-O_2 (b) cells at 250 mA g⁻¹.



Fig. S6. The electrochemical performance of Li-O₂ cell using lithium metal, (a) charge and discharge curves, (b) the capacity and terminal discharge voltage versus cycle number.



Fig. S7. The electrochemical impedance spectroscopy (EIS) of fresh Li-O_2 cell and those with different cycles at charging state (a) and Si || Li_3N full cell with different cycles at charging state (b).



Fig. S8. SEM images of lithium metal anode in Li-O₂ cell after 60 cycles (a), fresh Si anode (b) and Si anode in Li_xSi-O₂ cell after 100 cycles (c).