

Supporting Information

A long-life Na-air battery based on soluble NaI catalyst

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S1 Experimental

Assembly and Electrochemical measurements

A carbon nanotube (CNT, Chengdu Organic Chemicals Co. Ltd) /Ni electrode was used as air electrode for the electrochemical tests in this work. The CNT powder was dispersed in ethanol and then cast onto the Ni foam, followed by drying at 75 °C for 24 h. A pure carbon cloth (Shanghai Hesun Electrical Co. Ltd, 130 g m⁻², the surface area 1 cm²) electrode was used for comparison. The pure carbon cloth was immersed in ethanol for 10-15 min and dried at 75 °C for 24 h. The CNT/Ni and carbon cloth cathodes were obtained after cooling the corresponding materials to room temperature.

The assembly of the cell has been described in detail in our recent work [11]. A conventional two-electrode cell was constructed in the dried air filled glove box with the CNT/Ni as the cathode and one sheet of high-purity sodium foil as the anode. Two kinds of liquid electrolytes were used - one is 1.0 M NaClO₄ in a nonaqueous solution of 1,2-dimethoxyethane (DME) as pristine electrolyte and another is the pristine electrolyte with the addition of 0.001 M NaI. Charge-discharge measurements were performed at room temperature with a Land BT 1-40 battery test system. All discharge/charge capacities were calculated based on the weight of CNT and NaI, which was examined by electrobalance (BP211D, Sartorius). The discharge capacities of pure carbon cloth and CNT/Ni air electrodes in Na-air battery had been calculated based on the mass of pure carbon cloth and CNT, respectively.

Physical characterization

Field-emission transmission electron microscopy (FETEM) and selected-area electron diffraction measurements (SAED) were carried out in a 200 kV side entry JEOL 2010 TEM. Raman spectra were obtained on a HORIBA Jobin Yvon XploRA-FDU USING He-Ne laser light source (632.8nm). *Ex situ* TEM and SAED measurements were collected from air electrodes after initial discharge and charge process. The model cells were disassembled in an Ar-filled glove box and the air electrodes were rinsed by DMC for several times to remove the residual sodium salts. To avoid any exposure of air electrodes to oxygen or water, they were rapidly transferred into the chambers for characterization. For Raman measurement, the electrodes were enclosed in a sealed container covered by a thin and transparent glass slide.

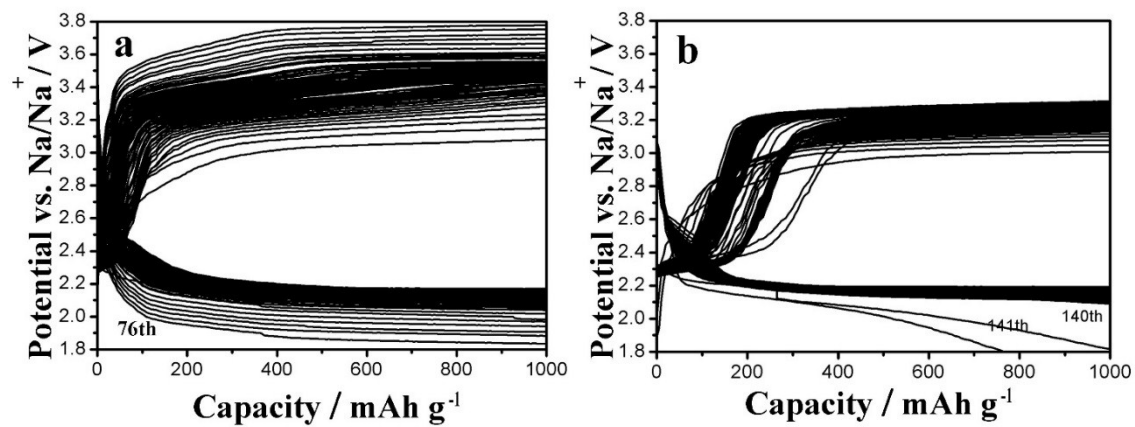


Figure S1. Cyclic performances of Na-air batteries using (a) 0.005M and (b) 0.01M NaI-containing electrolytes (the capacity was limited to 1000 mAh g⁻¹).

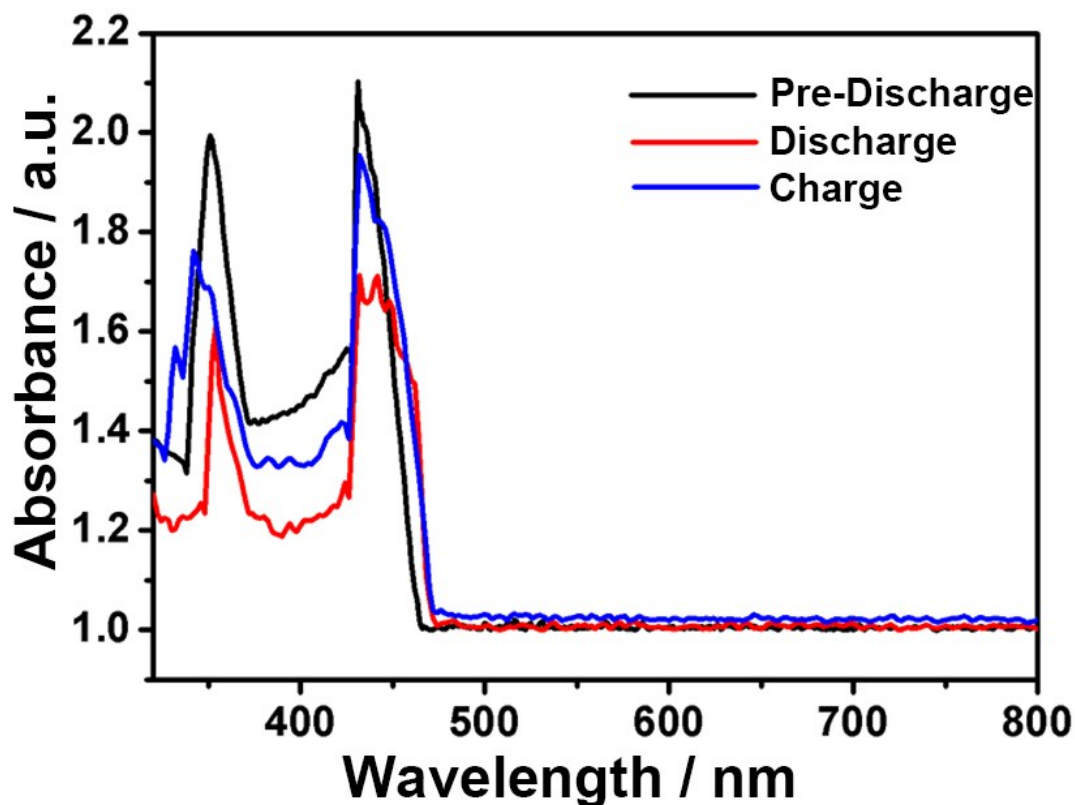


Figure S2. The UV Spectrophotometry of iodine ion in 0.05M NaI-containing electrolytes before discharge, after discharge, after charge, respectively

We have tested the UV absorption spectra of iodine ion in electrolyte according to the Reference (J. Braz. Chem. Soc., Vol. 9, No. 2, 171-174, 1998.). The specific methods is as follows: Firstly a certain amount of potassium iodate (0.006M) are added into 0.05M NaI-containing electrolytes, the electrolytes after the discharge and charge 150 cycles, respectively. Then these electrolytes are diluted above 1000-fold with DME. The UV spectrophotometry was used to determine the absorbance of iodine ion concentration in these electrolytes. As shown in **Figure S2**, the curve in 352 nm can be attributed to the absorption peak of I_3^- . The absorbance of I_3^- in the electrolyte decreases after 150 cycles, indicating the loss of iodine during the cyclic process.

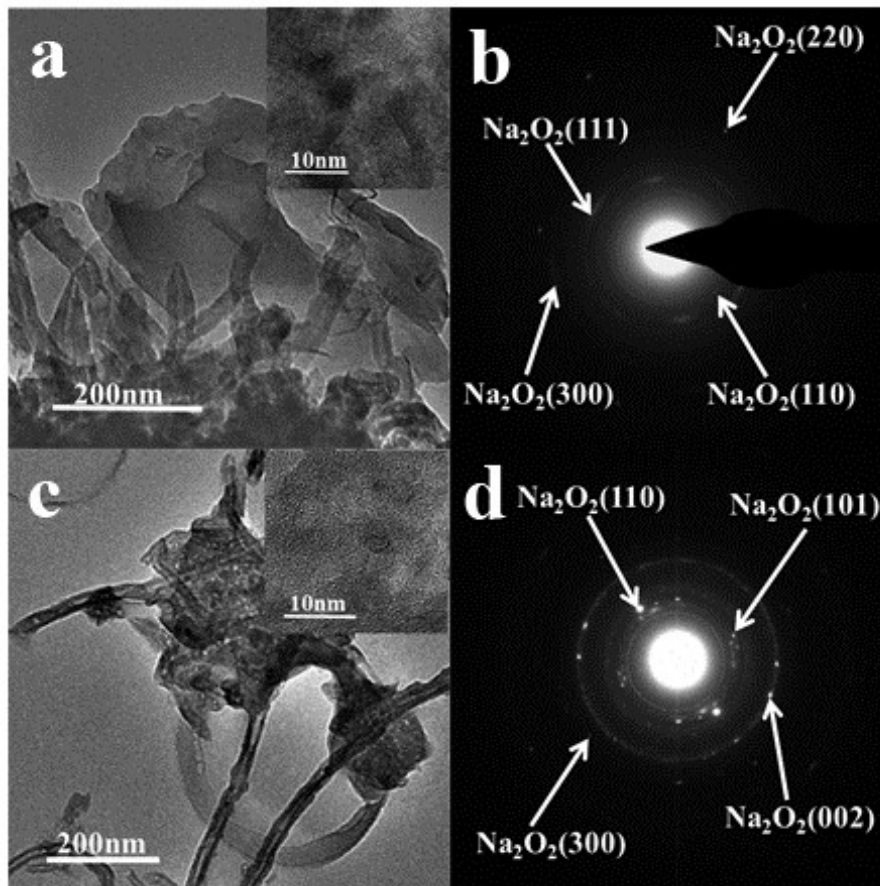


Figure
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S3. The HRTEM images and SAED patterns of air electrodes in the Na-air batteries with (a) 0.001M and (b) 0.10M NaI-containing electrolyte.

From the HRTEM image, the morphology of the discharge product in the Na-air batteries with 0.001M NaI-containing electrolyte is similar to that 0.01M NaI-containing electrolyte. All diffraction d-spacings in the SAED pattern can be well indexed to the hexagonal Na_2O_2 (JCPDS Card No.74-111). These results confirm that the same discharge product of Na_2O_2 could be found in Na-air batteries with various concentrations of NaI-containing electrolyte.

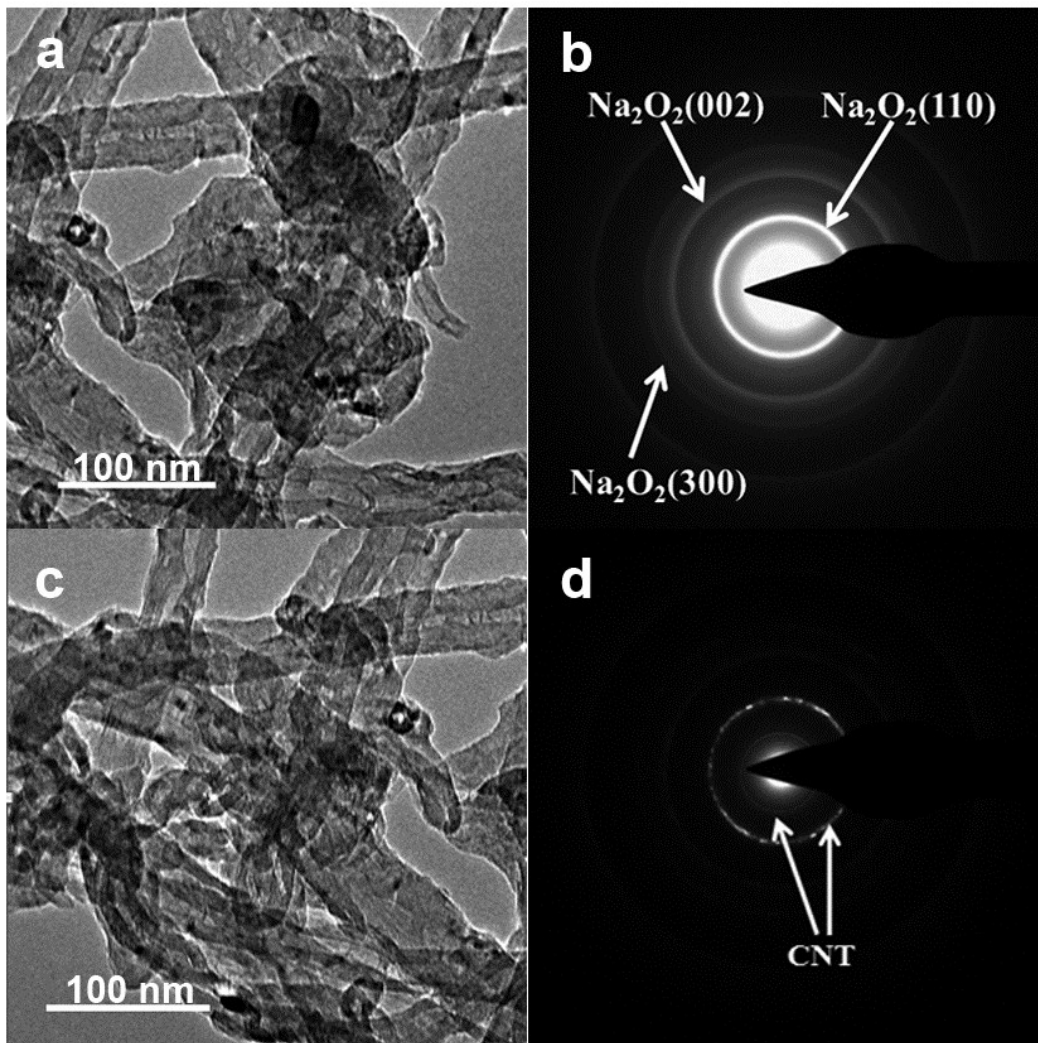


Figure S4. The HRTEM images and SAED patterns of the discharge (a,b)/charge(c,d) products on the air electrode in 0.05 M NaI-containing electrolyte after 150 cycles.

These results showed that the discharge products of Na_2O_2 on the air electrode in 0.05 M NaI-containing electrolyte after 150 cycles is found and Na_2O_2 disappears when the cell is charged to 3.3 V.

Table S1. Cyclic performances of Na-air batteries reported recently

Battery System	Discharge Product	Air Electrode	Discharge Capacity / mAh g ⁻¹	Current Density / mA g ⁻¹	Cycle Number	Reference
Na-O ₂	Na ₂ O ₂	DLC	1050-2100	1/10 C	20	1
Na-O ₂	Na ₂ O ₂	GNS	1150	75	3	2
Na-O ₂	Na ₂ O ₂	NGNS	1150	75	3	2
Na-O ₂	Na ₂ O ₂	GNS	1200	300	10	3
Na-O ₂	Na ₂ O ₂	CF _x	1000	200	6	4
Na-O ₂	Na ₂ O ₂ ·2H ₂ O	CNT	1000	500	7	5
Na-O ₂	Na ₂ O ₂	NiCo ₂ O ₄	1000	50	10	6
Na-CO ₂ /O ₂	NaHCO ₃	Porous Carbon	800	200	20	7
Na-O ₂	NaO ₂	GDL	64	200 μA cm ⁻²	80	8
Na-O ₂	NaO ₂	Ketjenblack	1666	200 μA cm ⁻²	60	8
Na-O ₂	NaO ₂	VACNT	750	67	130-140	9
Na-O ₂	Na ₂ O ₂	Ni/CNT	1000	500	150	This work

Reference

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