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Na-CO Battery: a Device to Trap CO

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This PDF file includes: Materials, Methods, Fig. S1 to S14.

Table of contents

Experimental section

Materials

The solvent tetraethylene glycol dimethyl ether (TEGDME) is purchased from Aladdin. Before to use, it is treated by Na metal and collected by reduced pressure distillation and then stored with activated 4 Å molecular sieves (beads 8-12mesh, J&k) in glove box (H_2O and O_2 < 0.1 ppm). The solvent has a final water content below 4 ppm. $NaClO_4$ (anhydrous, Alfa Aesar) are dried under vacuum at 120 °C for 10 hours. Multi-wall carbon nanotubes (MCNTs) is supplied by Cnano Technology Ltd. and carbon paper is from Alfa.

Methods

Cathode fabrication

The cathode of MCNTs on carbon paper without any binder is prepared using a spraying process. The slurry containing 50 mg MCNTs in 50 mL ethanol is sonicated for approximately one hour. Then the uniform slurry is spraying onto one piece of carbon paper ($10 \times 10\ cm^2$) with a power gas of high-pressure air. The heat board at 100 °C ensures the immediate drying of ethanol and make MCNTs firm on carbon paper. The obtained carbon cathode is dried in a vacuum oven at 60 °C overnight. The cathode electrode is 10 mm in diameter and the loading MCNTs is 0.5 mg/cm^2. The Vulcan XC-72 carbon cathode is prepared in the same method as above. Au cathode is fabricated by spraying the Au particle to the surface of nickel foam.

Battery assembly

The coin-type CR-2032 cells are assembled by using Na anode (ϕ=10 mm), glass fiber as separator and MCNTs cathode in an argon-filled glove box. The electrolyte is 1M $NaClO_4$ in TEGDME. The cathode case is predrilled with seven homogenously distributed holes to allow the diffusion of CO. Then the batteries were put into a glass vessel (250 mL) filled with high pure CO (1 bar). Before electrochemical testing, the batteries are rested for 10 h.

Characterization

X-Ray diffraction (XRD) analysis between 15-60° was performed on a Rigaku MiniFlex600 with Cu-Kα radiation (λ = 1.54178 Å) with a step rate of 0.02°/s. The morphology and structure were investigated by field-emission scanning electron microscopy (SEM, JEOL JSM7500F) and transmission electron microscopy (TEM, Philips Tecnai-F20). Fourier transform infrared (FTIR) spectroscopy was collected by using Tensor II (Bruker) at a resolution of 4 cm^{-1}. Raman spectroscopy was observed with a Thermo-Fisher Scientific (excitation wavelength, 532 nm). X-ray photoelectron (XPS) spectroscopy was measured in a Versa Probe PHI 5000 system (Al Kα radiation of 1486.6eV).

Electrochemical testing

Galvanostatic discharge/charge tests were performed on a LAND battery-test instrument (CT2001A). The current density and specific capacity were based on the mass of MCNTs. Cyclic voltammetry was conducted on a CHI660B electrochemical workstation at a scan rate of 0.05 mV/s. Electrochemical impendence spectra (EIS) is measured on a Parstat 2273A potentiostat/galvanostat workstation (AMETEK Company) in the frequency of 100 mHz to 100 kHz.

Solubility test of sodium carbonate

We have conducted the inductively coupled plasma (ICP) test to calculate the concentration of Na^+ in electrolyte before and after Na_2CO_3 addition. The concentration of original Na^+ in electrolyte is 122.4385 g/L. After adding Na_2CO_3, the concentration of Na^+ is nearly unchanged (122.4389 g/L), indicating that Na_2CO_3 could not be dissolved into the electrolyte.

CO_2-evolution test

Gas evolution is tested by GC-2010 Plus (SHIMADZU) with an AOC-20i auto injector and flame ionization detectors, stabilwax capillary column (30 m × 0.32 mm, film thickness of 0.5 μm) at temperatures ranging from 25 °C to 160 °C, with a gradient of 10 °C/min and injector temperature of 250 °C; helium as carrier gas at a flow rate of 30 mL/min, splitless injection, electron impact of 70 eV, and ion source temperature of 250 °C. The charging atmosphere was identified based on retention indices, which are determined by the compounds retention time in capillary column.

Firstly, the battery discharged to 1000 mAh/g in pure CO atmosphere. Then, the battery charged to 1000 mAh/g. The gas atmosphere was tested by gas chromatography. The second and third cycle tests were carried on in turn. The theoretical value of CO_2 is calculated based on reaction:

$$C + 2Na_2CO_3 \rightarrow 3CO_2 + 4Na \qquad (1)$$

The electric quantity about 1000mAh/g can be described as:

$$Q=3.6 \times C \times m \qquad (2)$$

where C is the specific capacity (1000 mAh/g), m is the weight of MCNTs on an electrode plate (0.3925×10^{-3} g). The obtained electric quantity is 1.413 C.

The electron transfer mole number (n) was obtained by equation:

$$n = \frac{Q}{F} \qquad (3)$$

where F is Faraday′s constant (96485 $C \cdot mol^{-1}$). So,

$n = 1.46 \times 10^{-5}$ mol.

Theoretically, the amount of evolved CO_2 relates to the transferred charges following a 3:4 ratio. Via ideal gas Law and bottle volume (V=250 mL), the concentration of CO_2 can be calculated using the following equation：

$$\mathrm{ppm}(CO_2) = \frac{3 \times n \times V_m}{4 \times V} \times 1000000 \qquad (4)$$

where V_m is the molar volume of gas at STP (22.4 L/ mol). The obtained theoretical

CO_2 concentration is 981.12 ppm.

Theoretical specific energy density calculations

The discharge reactions of Na-CO battery can be described as equation (5):

$$Na + 3/2CO \rightarrow 1/2Na_2CO_3 + C\text{, } E_{ocv}\text{=3.28 V} \qquad (5)$$

where E_{ocv} is the open circuit voltage (OCV) at standard conditions (25 °C, 1.0 atm). The theoretical specific energy density of Na-CO battery $E^{W}_{\mathrm{Na}-CO}$ is calculated using the following equation:

$$C^{W}_{Na-CO} = \frac{nF}{w_{Na} + 3/2w_{CO}} \qquad (6)$$

$$E^{W}_{Na-CO} = C^{W}_{Na-CO} \cdot E_{OCV} \qquad (7)$$

where C^{W}_{Na-CO} is the theoretical specific capacity based on the total active materials, n is the battery reaction electron number (n=1), F is the Faraday's constant (96485 A·s mol^{-1}), w_{Na} and w_{CO} are the weight of one mole of Na metal (22.99 × 10^{-3} kg·mol^{-1}) and CO (28 × 10^{-3} kg·mol^{-1}) respectively. The obtained theoretical specific capacity and energy density for a Na-CO battery are 412.39 mAh/g and 1352.6 Wh·kg^{-1} respectively.

Actual specific energy density calculation based on total active materials (Na and CO).

The mass of total active materials can be calculated using the following equation:

$$m = \frac{C \times m_{MCNTs}}{F}\left(w_{Na} + \frac{3}{2} w_{CO} \right) \tag{8}$$

where m_{MCNTs} (0.3925 mg) is the mass of MCNTs, C (8000 mAh·g^{-1}) is the specific capacity for the active material (m_{MCNTs}) of cathode, F is the Faraday's constant (26.802 Ah·mol^{-1}), w_{Na} and w_{CO} are the weight of one mole of Na (22.99 g·mol^{-1}) and CO (28 g·mol^{-1}) respectively. The calculated mass of total active materials (Na and CO) is 7.6151 mg.

The actual specific energy density is calculated by the following equation:

$$E = \frac{C \times m_{MCNTs}}{m} \times V \tag{9}$$

where V (~2.1 V) is the average operation voltage of the electrical discharge. The obtained actual specific energy density is 865.9 Wh·Kg^{-1}.

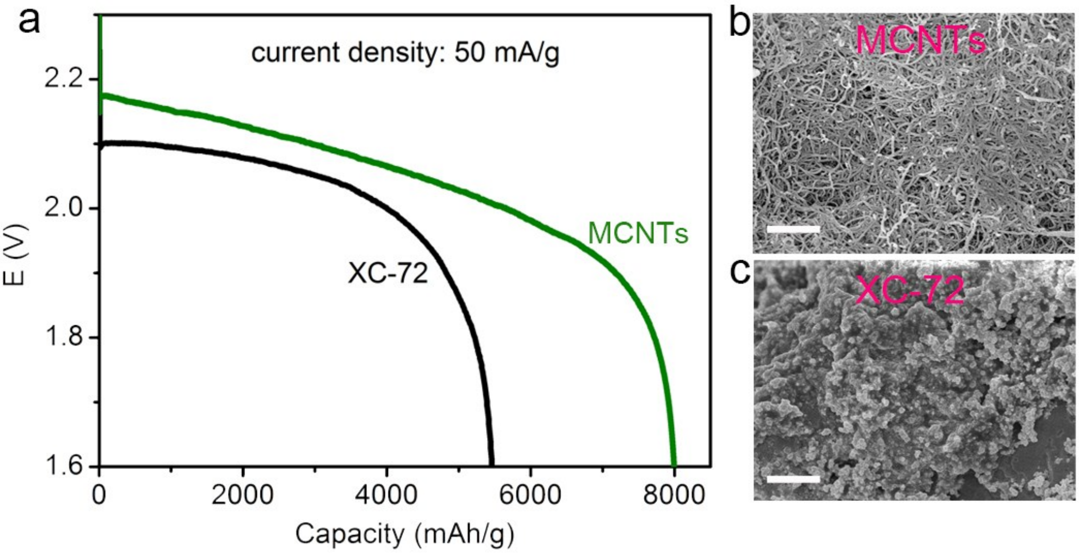

Fig. S1. (a) The initial discharge profiles of Na-CO battery using MCNTs and XC-72 as cathode, respectively. SEM images of (b) MCNTs and (c) XC-72 electrode. The scale bar is 1μm.

MCNTs and XC-72 are used to make a comparison on the electrochemical properties of Na-CO battery. When using MCNTs as cathode, the battery shows larger discharge capacity and lower discharge overpotential than that of using XC-72 (Fig. S1). This attributes to the aligned cross-linked three-dimensional morphology of MCNTs (Fig. 1c, d and Fig. S1b), which is favorable for electrolyte wetting, gas diffusion, discharge products depositing and electron transportation. However, XC-72 electrode shows more aggregated carbon particles (Fig. S1c), which is disadvantage for gas diffusion.

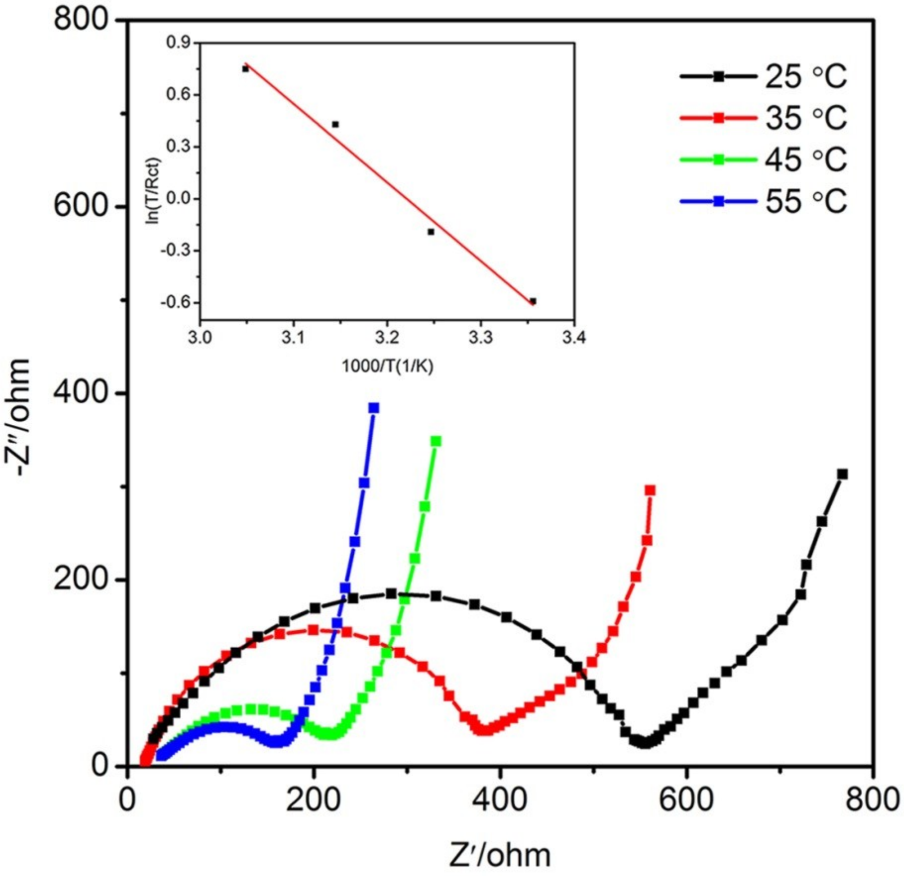

Fig. S2 Electrochemical impedance spectra (EIS) of Na-CO battery at different temperature and the Arrhenius plots (inset).

EIS result confirms that the battery has a lower charge transfer resistance (R_{ct}) at high temperature. The activation energy (E_a) can be calculated from the following equation $i_0 = RT/(nFR_{ct}) = A\ exp(-E_a/(RT))$, where i_0 is the exchange current, R is the universal gas constant, A is a temperature-independent coefficient, and T is the absolute temperature. The calculated activation energy is 37.7 kJ/mol, as determined from the Arrhenius plots.

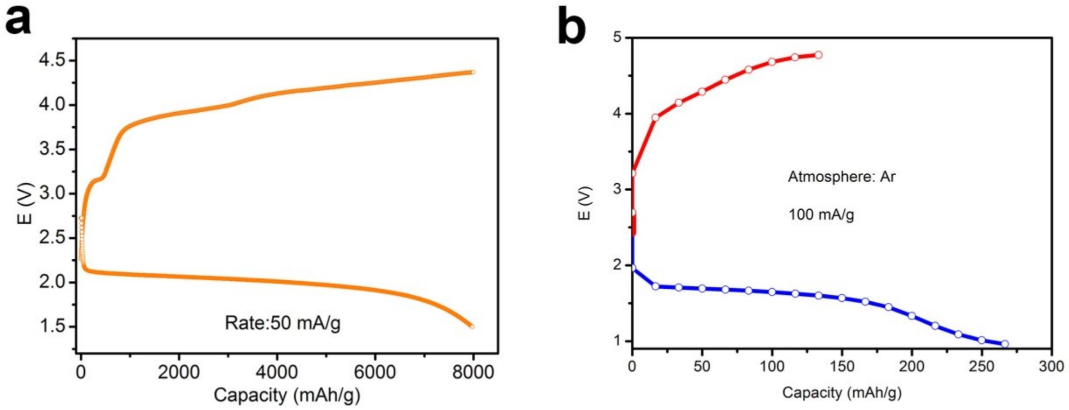

Fig. S3 (a) The first deep discharge/charge profiles of Na-CO battery at current density of 50 mA/g. (b) The discharge/charge profiles of Na-CO battery at Ar atmosphere. The discharge/charge curves of this battery in argon display the electrochemical window is between 1.2 V and 4.5 V, within which the electrolyte $NaClO_4$-TEGDME is stable.

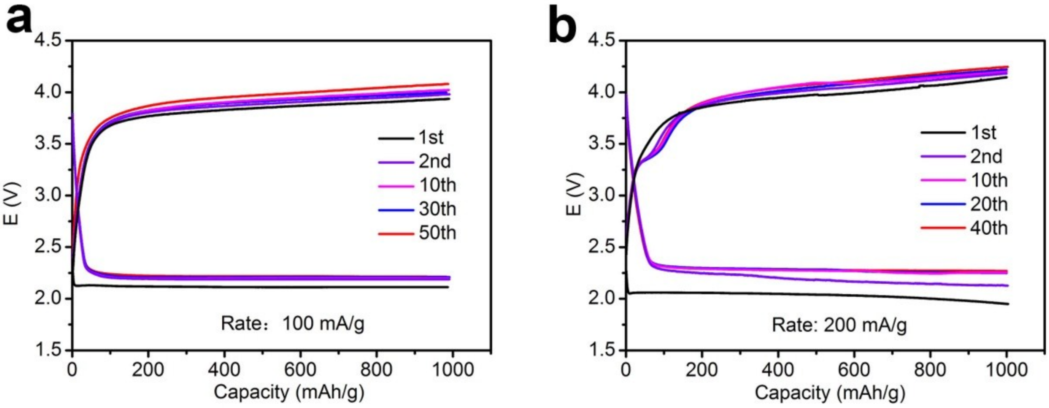

Fig. S4 Discharge-charge profile of Na-CO battery at a current density of 100 mA/g and 200 mA/g with curtailing capacity of 1000 mAh/g, respectively.

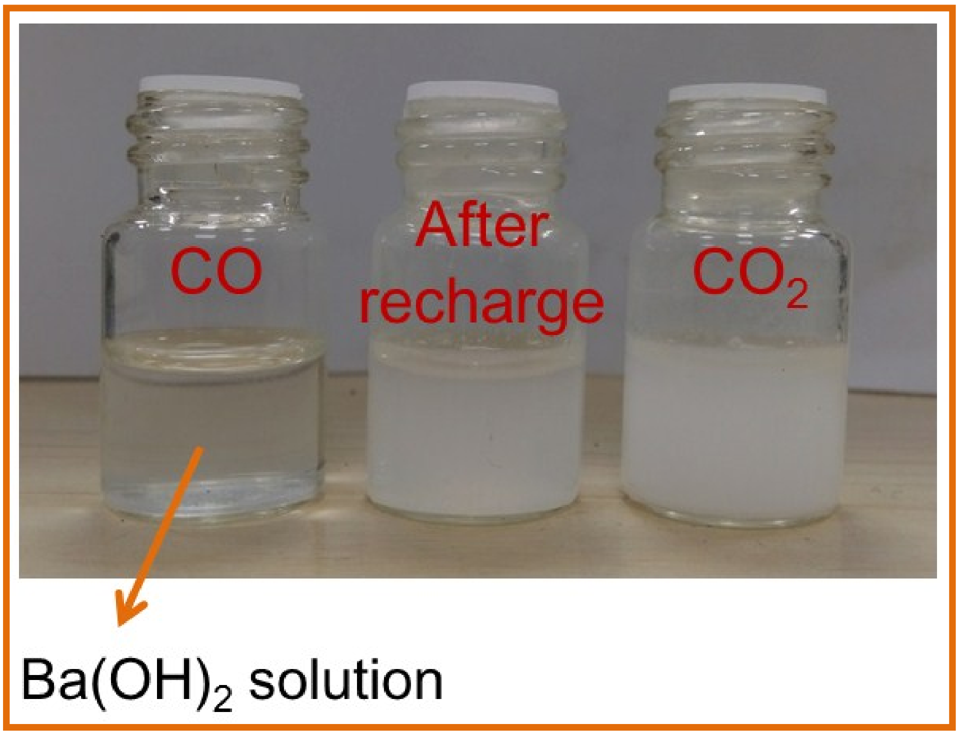

Fig. S5 The test of gas atmosphere by bubbling the gas into $Ba(OH)_2$ solution.

When the gas after recharge is bubbling into $Ba(OH)_2$ solution, milk white precipitation is immediately formed.

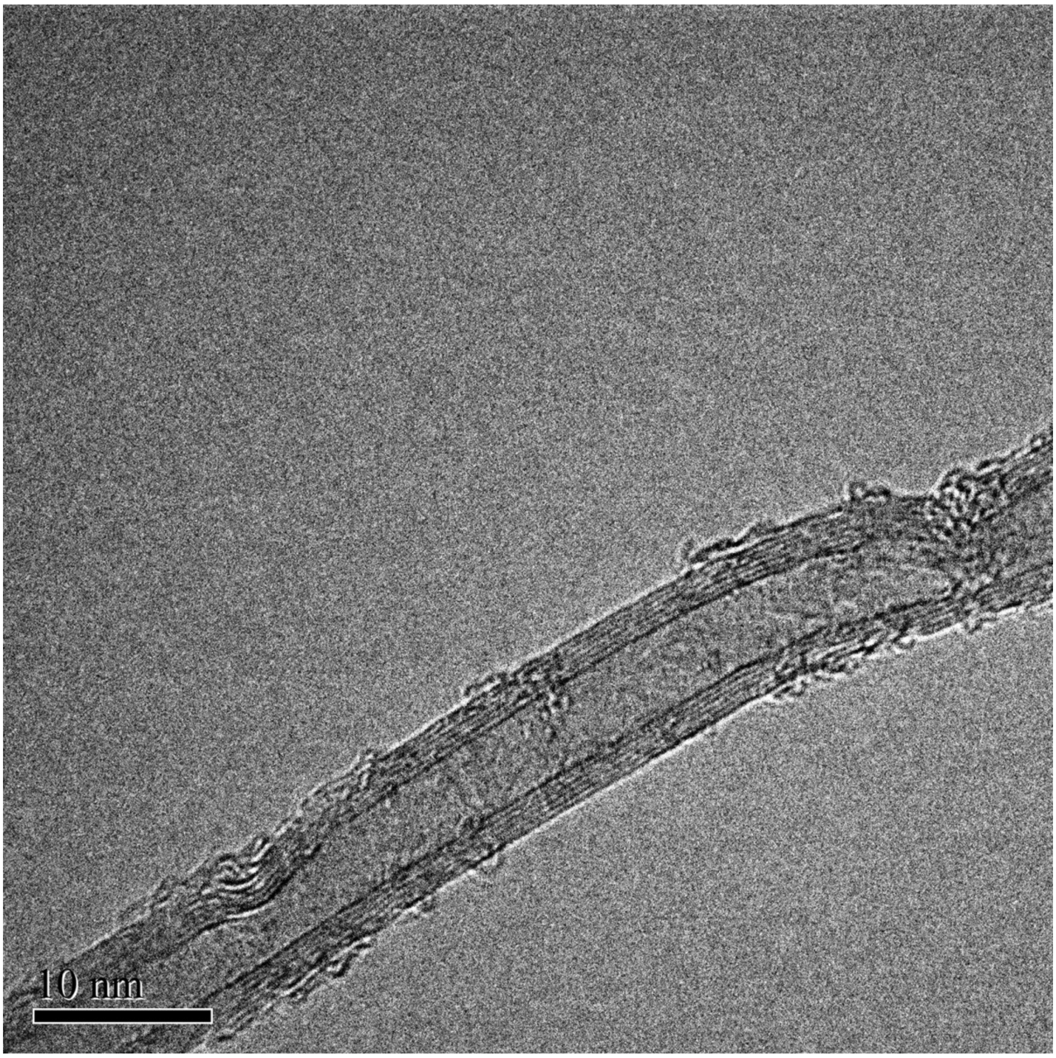

Fig. S6 High resolution transmission electron microscopy (HRTEM) image of MCNTs after the charging process.

The boundaries of the carbon nanotubes are clear and the walls are still integrated and do not appear any destruction.

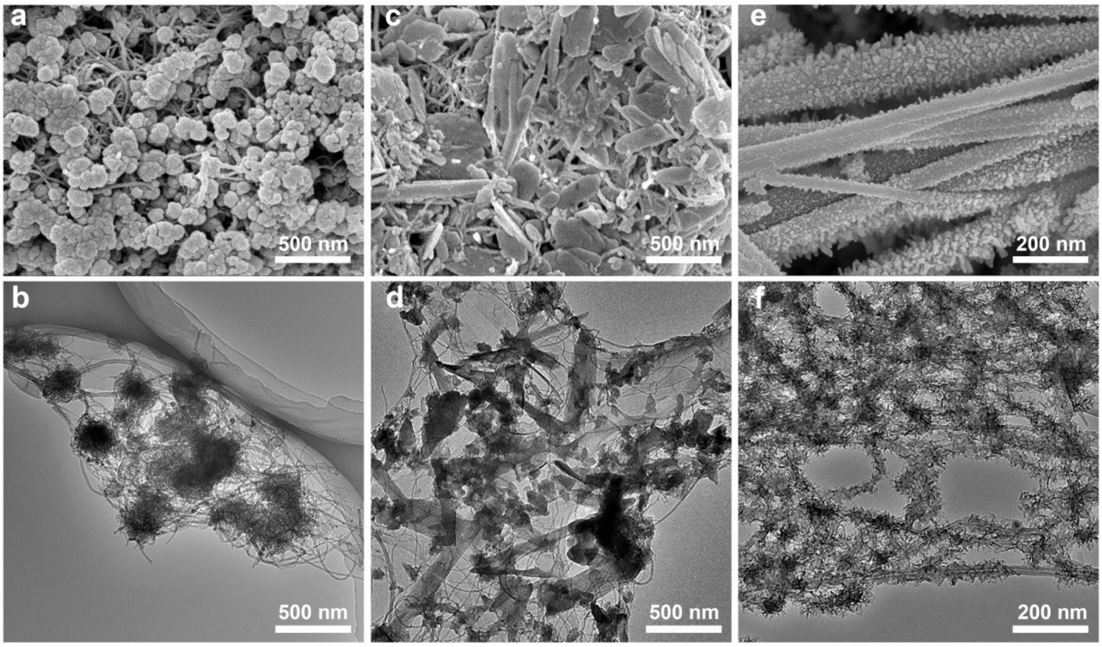

Fig. S7 SEM and TEM images of MCNTs cathode in the processes of discharge at different temperatures: 35 °C (a and b), 45 °C (c and d), 55 °C (e and f).

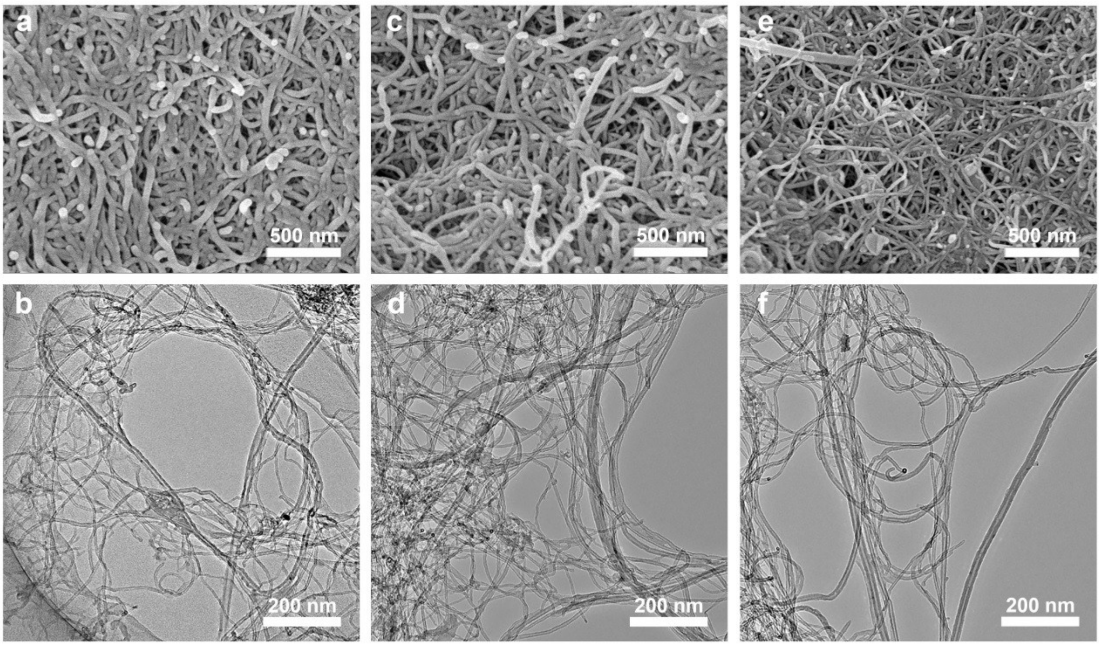

Fig. S8 SEM and TEM images of MCNTs cathode in the processes of recharge at different temperatures: 35 °C (a and b), 45 °C (c and d), 55 °C (e and f).

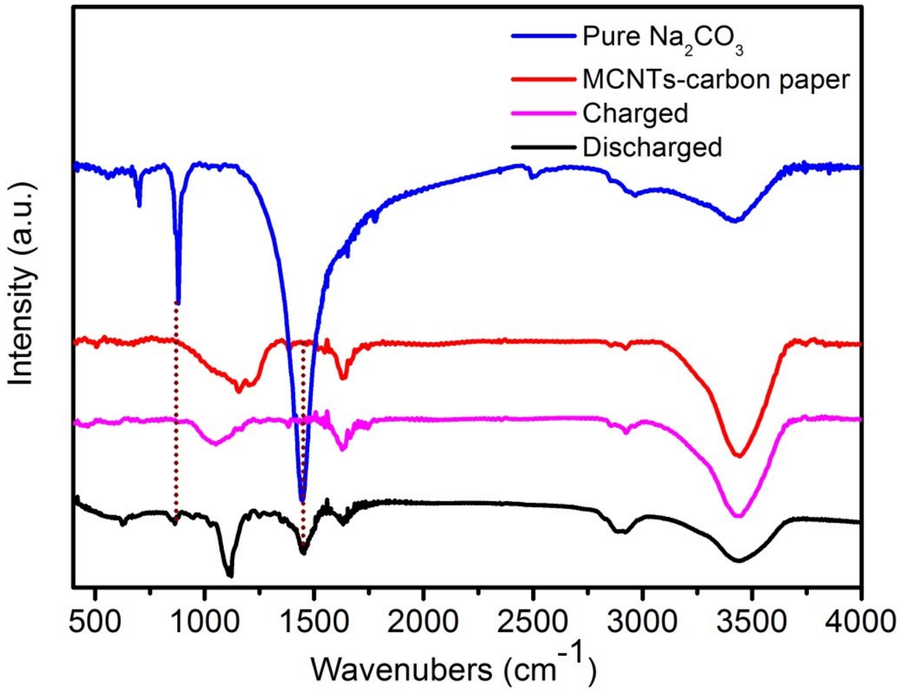

Fig. S9 FT-IR of the MCNTs cathode at different states.

As the FTIR spectra shown, we have characterized the discharge and charge products respectively. Compared with the commercial Na_2CO_3, we have observed the stretching vibration peaks (~1442 cm^{-1}) and bending vibration peaks (~880 cm^{-1}) of Na_2CO_3 after discharged, which disappeared after charging. This result has testified that Na_2CO_3 is the major discharge product. The rest strong peaks contain characteristic peaks (~1630 and ~1150 cm^{-1}) of MCNTs-carbon paper.

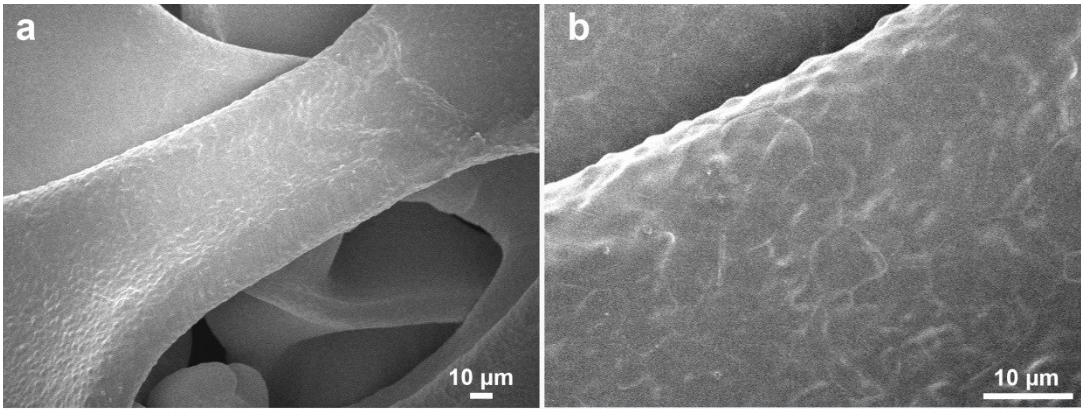

Fig. S10 SEM images of pristine Au on Ni foam electrode.

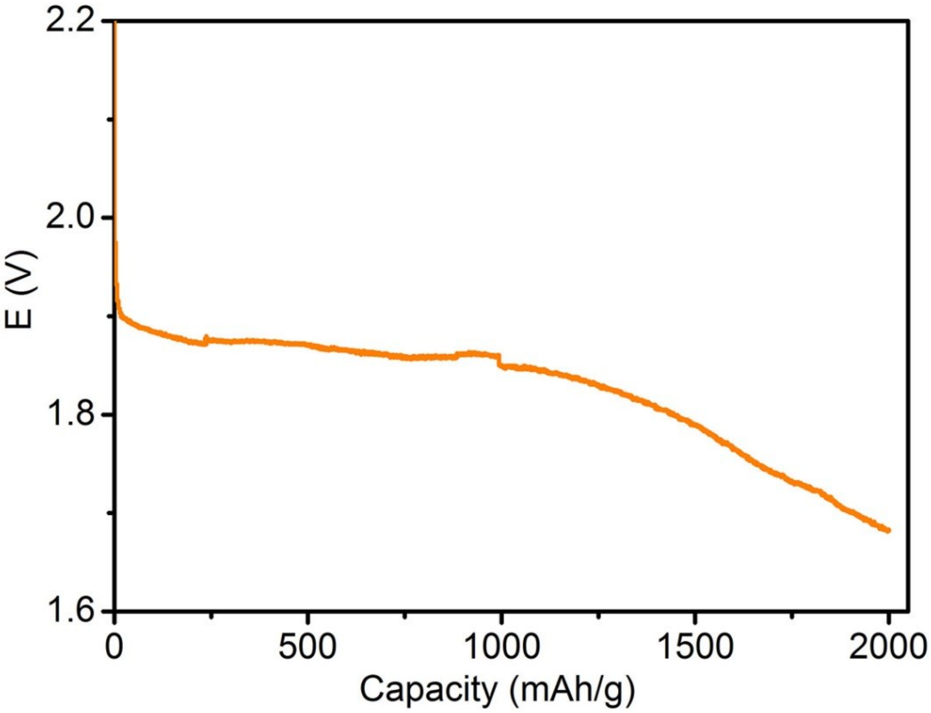

Fig. S11 Discharge curves of Na-CO batteries used Au cathode with capacity of 2000 mAh/g at 50 mA/g.

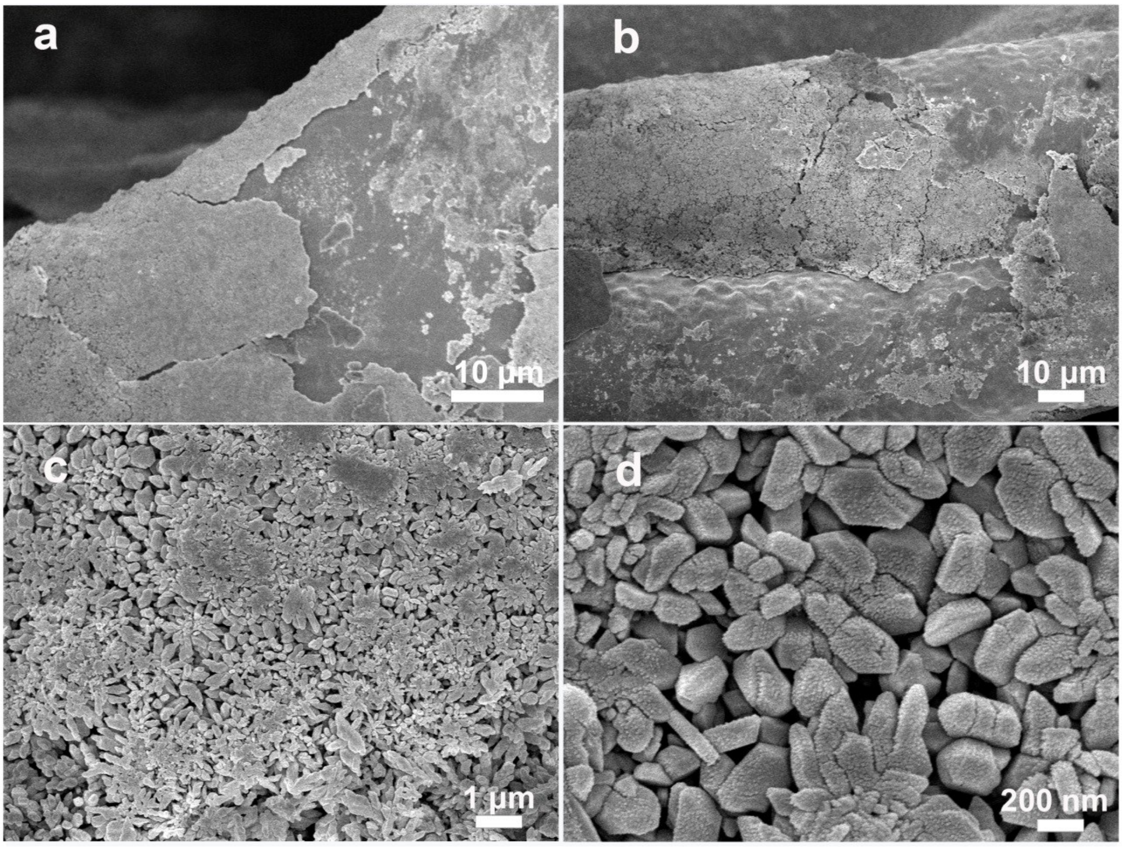

Fig. S12 SEM images of discharge product on the Au cathode.

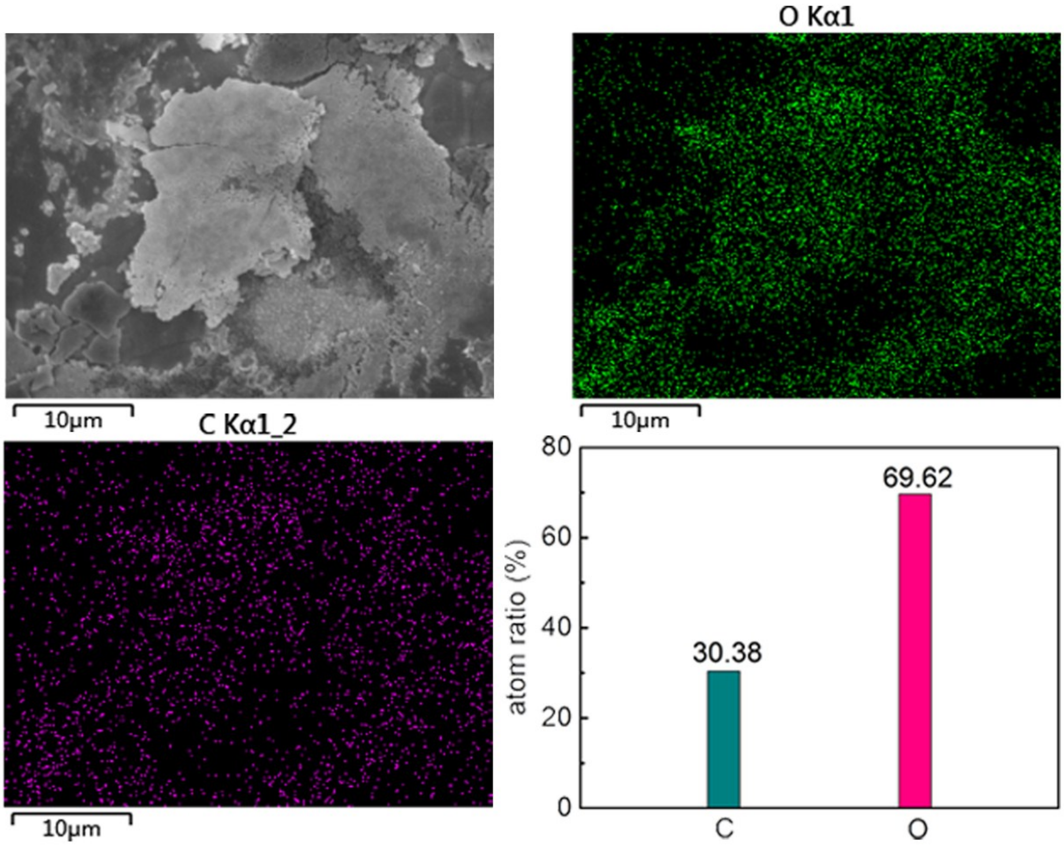

Fig. S13 EDX elemental mapping images of the discharge products on Au electrode and the atom ratio of C and O.

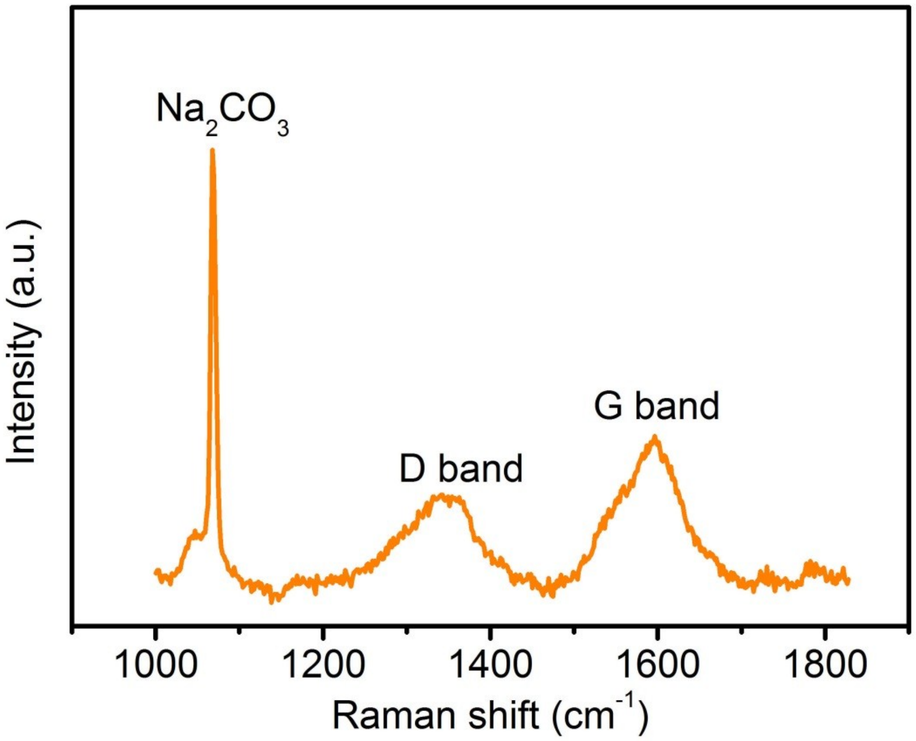

Fig. S14 Raman spectra of Au cathode with discharge capacity of 2000 mAh/g in Na-CO battery.