Supporting Information

Long-Life Na-O_2 Batteries with High Energy Efficiency Enabled by Electrochemically Splitting NaO_2 at Low Overpotential

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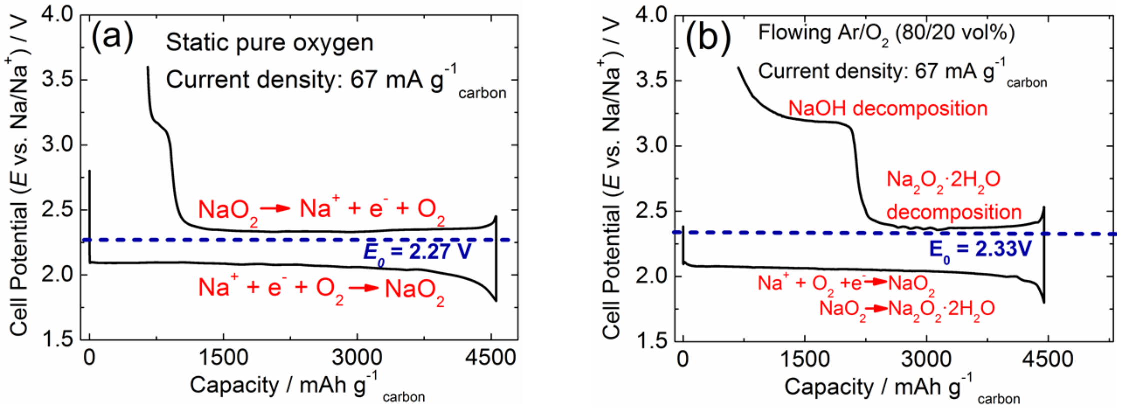

Figure S1. The typical discharge and charge curves of Na-O_2 batteries operated under (a) the static pure O_2 atmosphere and (b) the flowing Ar/O_2 (80/20 vol%) atmosphere. The batteries were tested at a current density of 67 mA g^{-1}_{carbon} (~0.1 mA cm^{-2}) within a voltage range of 1.8-3.6 V. The specific capacity is calculated based on the mass of carbon in the VACNT cathodes. E_0 = 2.27 V denotes the thermodynamic potential based on the reaction of $Na^+ + e^- + O_2 \rightarrow NaO_2$. E_0 = 2.33 V denotes the thermodynamic potential based on the reaction of $2Na^+ + 2e^- + O_2 \rightarrow Na_2O_2$. The reaction formulae are given according to the distinctive discharge/charge plateau potentials in combination with the phase analysis by XRD. Note that NaO_2 is the main discharge solid product in the static atmosphere, whereas it is $Na_2O_2{\cdot}2H_2O$ in the flowing atmosphere. It indicates that the discharge products and recharge curve profiles greatly depend on the working atmospheres.

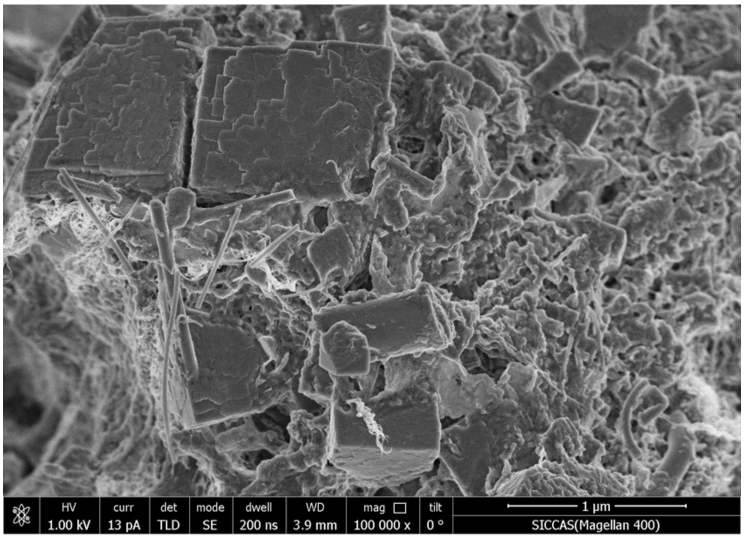

Figure S2. SEM image for the NaO_2 particle consisting of stacked thin plates wired by carbon nanotubes.

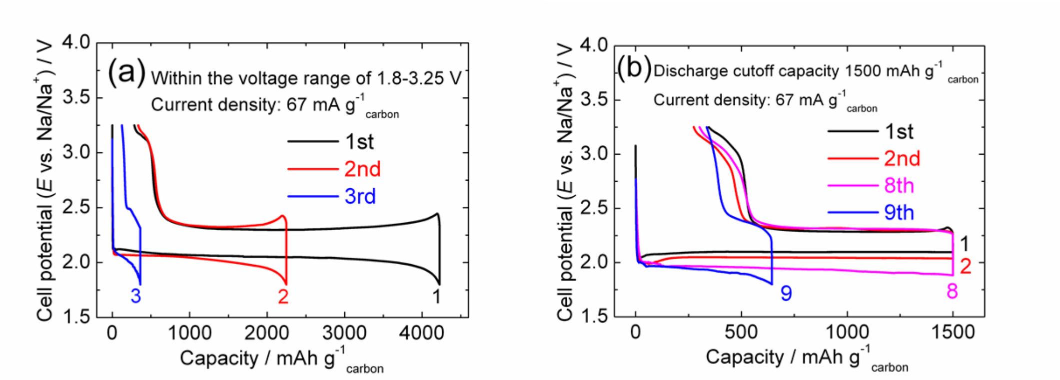

Figure S3. Cycleability as a function of discharge depth for the Na-O_2 batteries under the flowing Ar/O_2 (80/20 vol%) atmosphere. (a) Cycling curves for the NaO_2 batteries tested within a voltage range of 1.8-3.25 V. (b) Cycling curves for the NaO_2 batteries tested with a cutoff discharge capacity of 1500 mAh g^{-1}_{carbon} and a cutoff charge voltage of 3.25 V. The current density for all the tests is 67 mA g^{-1}_{carbon}. For the case of full discharge, the capacity decreases drastically during the first three cycles. The released capacity during the 3rd discharge is smaller than 10% of the first discharge capacity. In the case with a cutoff discharge capacity of 1500 mAh g^{-1}_{carbon}, eight cycles without the loss of initial capacity can be maintained. The capacity is approximately 45% of the initial value at the 9th discharge.

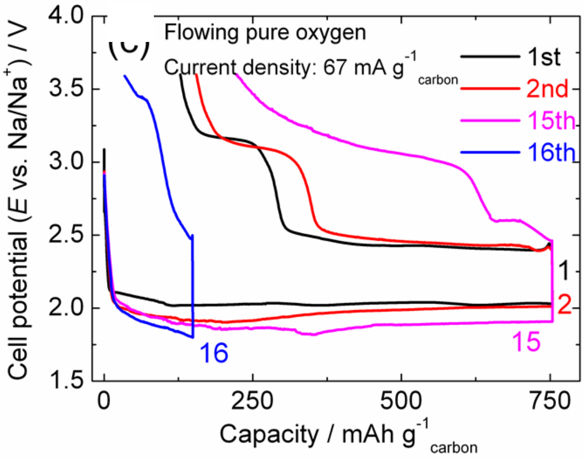

Figure S4. Cycleability of the Na-O_2 battery operated in the flowing pure O_2 atmosphere with a cutoff discharge capacity of 750 mAh g$^{-1}_{carbon}$ and a charge voltage of 3.6 V at the current density of 67 mA g$^{-1}_{carbon}$. Although fifteen cycles without the loss of initial capacity can observed, the curve profiles are not stable and change a lot especially for the charge process. The capacity fades seriously from the 16th cycle.

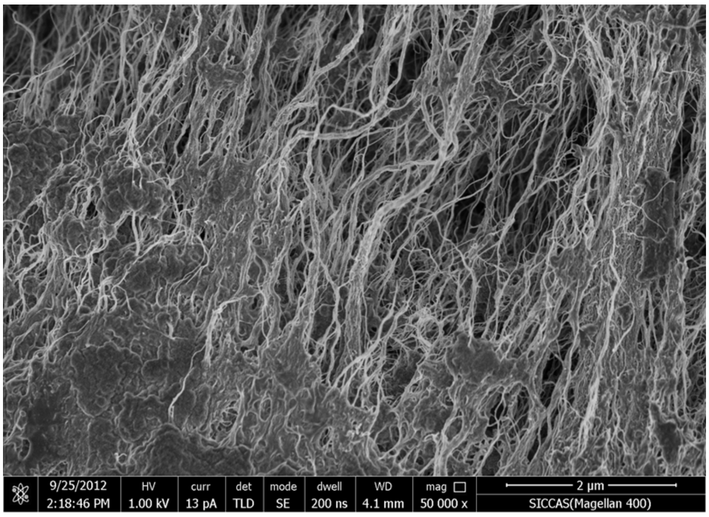

Figure S5. Overview SEM image for the VACNTs cathode disassembled from the Na-O_2 battery operated under the flowing pure O_2 atmosphere after full discharge (D, as shown in Figure 2b).

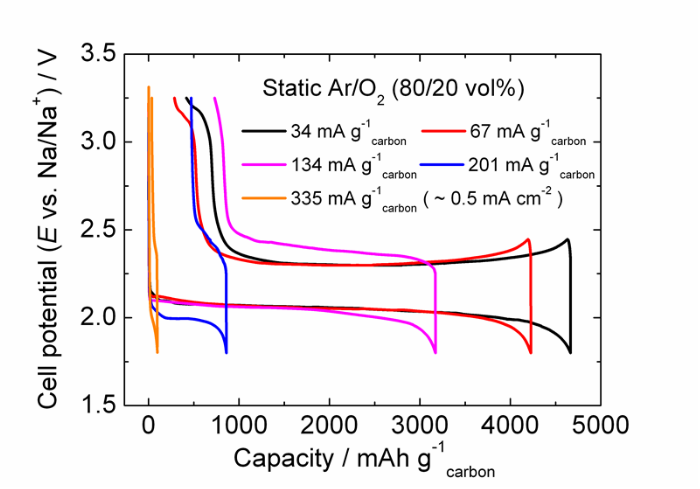

Figure S6. Rate performance of the Na-O$_2$ batteries without a pre-discharge process at low rate in the static Ar/O$_2$ (80/20 vol%) atmosphere.

Calculation of the thermodynamic potential based on the reaction

$$NaOH \rightarrow Na^+ + e^- + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2\uparrow$$

The thermodynamic potential E_0 of the reaction

$$NaOH_{solid} \rightarrow Na^+ + e^- + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2\uparrow$$

$$NaOH_{aqueous} \rightarrow Na^+ + e^- + \tfrac{1}{2}H_2O + \tfrac{1}{4}O_2\uparrow \qquad (1)$$

is calculated according to

$$\Delta G^0_{reaction} = -nFE_0 \qquad (2),$$

where n denotes the number of transferred electrons in the reaction (1), F is the Faraday constant, ΔG^0 is the Gibbs energy of the reaction (1) which can be obtained by

$$\Delta G^0_{reaction} = \sum \Delta G^0_{f(reactants)} - \sum \Delta G^0_{f(products)} \qquad (3),$$

where $\sum \Delta G^0_{f(products)} = \Delta G^0_{f(Na)} + \frac{1}{2}\Delta G^0_{f(H2O)} + \frac{1}{4}\Delta G^0_{f(O2)}$ = 0 + (-237.1 kJ mol^{-1})/2 + 0 = -118.55 kJ mol^{-1}, and $\sum \Delta G^0_{f(reactants)} = \Delta G^0_{f(NaOH_{solid})}$ or $\Delta G^0_{f(NaOH_{aqueous})} = -379.4\ kJ/mol_{solid}$ or $-419.20\ kJ/mol_{aqueous}$. Therefore, $\Delta G^0_{reaction}$ equates to $-260.85\ kJ/mol_{solid}$ or $-300.65\ kJ/mol_{aqueous}$ and $E_0 = -\Delta G^0_{reaction}/nF$ ≈ 2.70 V (for $NaOH_{solid}$) or 3.12 V (for $NaOH_{aqueous}$).

Calculations of the thermodynamic potential based on the reaction

$Na_2CO_3 \rightarrow 2Na^+ + 2e^- + \frac{1}{2}O_2\uparrow + CO_2\uparrow$

The thermodynamic potential E_0 of the reaction

$$Na_2CO_{3solid} \rightarrow 2Na^+ + 2e^- + \frac{1}{2}O_2 + CO_{2undissociated}$$

$$Na_2CO_{3aqueous} \rightarrow 2Na^+ + 2e^- + \frac{1}{2}O_2 + CO_{2undissociated} \qquad (1)$$

is calculated according to

$$\Delta G^0_{reaction} = -nFE_0 \qquad (2),$$

where n denotes to the number of transferred electrons in the reaction (1), F is the Faraday constant, ΔG^0 is the Gibbs energy of the reaction (1) which can be obtained by

$$\Delta G^0_{reaction} = \sum \Delta G^0_{f(reactants)} - \sum \Delta G^0_{f(products)} \qquad (3),$$

where $\sum \Delta G^0_{f(products)} = 2\Delta G^0_{f(Na)} + \frac{1}{2}\Delta G^0_{f(O2)} + \Delta G^0_{f(CO2)}$ = 0 + 0 + (-386.0 kJ mol^{-1}) = -386.0 kJ mol^{-1}, and $\sum \Delta G^0_{f(reactants)} = \Delta G^0_{f(Na_2CO_{3solid})}$ or $\Delta G^0_{f(Na_2CO_{3aqueous})} = -1044.4\ kJ/mol_{solid}$ or $-1051.6\ kJ/mol_{aqueous}$. Therefore, $\Delta G^0_{reaction}$ equates to $-658.4\ kJ/mol_{solid}$ or

$-665.6\ kJ/mol_{aqueous}$ and $E_0 = -\Delta G^0_{reaction}/nF \approx 3.41$ V (for Na_2CO_{3solid}) or 3.45 V (for $Na_2CO_{3aqueous}$).

The thermodynamic data (T = 298 K) is taken from Lange's Handbook of Chemistry, McGraw-Hill, 16th Edition, 2005

Calculation of the equivalent thickness of NaO_2 pre-deposition layer formed during the pre-discharge process

A pre-discharge at 67 mA g^{-1}_{carbon} for 1 h should yield an initial discharge capacity of 67 mAh g^{-1}_{carbon}. For the carbon mass of 1.5 mg cm^{-2} in VACNT cathode, the transferred charge ($Q_{transfer}$) should be 0.1 mAh cm^{-2}.

According to the reaction

$$Na^+ + O_2 + e^- \rightarrow NaO_2 \quad (1),$$

in combination with the Faraday rule we can obtain the relationship

$$\frac{m_{NaO_2}}{M_{NaO_2}} = \frac{Q_{transfer}}{F} \quad (2),$$

where m_{NaO_2} is the mass of NaO_2 (per cm^2) produced by the reaction (1), M_{NaO_2} is the relative molar mass of NaO_2 (54.99 g mol^{-1}), F is the Faraday constant (96485.3365 C mol^{-1}). Thus m_{NaO_2} is calculated to be 0.2 mg cm^{-2}. According to the theoretical density of NaO_2 (2.20 g cm^{-3}), the volume of NaO_2 per cm^2 is 9.1×10^{-5} cm^3.

It is known that the VACNTs are 1.5 mg cm^{-2} in mass with a specific surface area of 80 m^2 g^{-1}, the VACNTs per cm^2 should have the surface area of 1.2×10^3 cm^2

Consequently, the equivalent thickness of the NaO_2 layer uniformly deposited on VACNT surface is calculated to be $9.1\times10^{-5}\ cm^3/1.2\times10^3\ cm^2 = \sim1$ nm.