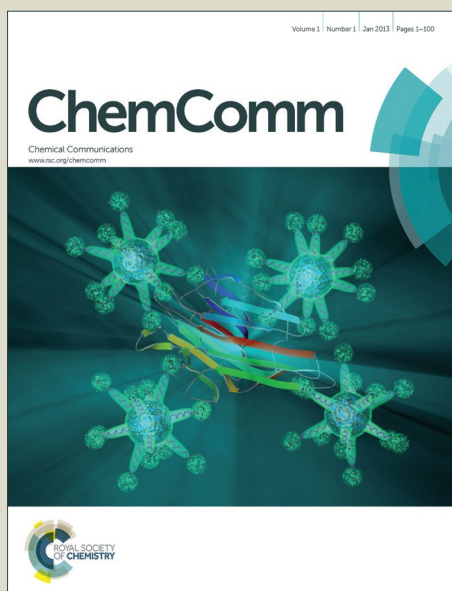# ChemComm

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

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Na-air battery with NaI dissolved in typical organic electrolyte could run up to 150 cycles with a capacity limit of 1000 mAh g^{-1}. The low charge voltage plateau of 3.2 V vs. Na$^+$/Na in Na-air battery should mainly be attributed to the oxidation reaction of active iodine anions.

In a nonaqueous Na-air battery, the Na$^+$ generated from metal sodium anode would react with O$_2^-$ or O$_2^{2-}$ at the air cathode through an electrolyte to form NaO$_2$ [1-6] or Na$_2$O$_2$ [7-12] during discharge process. These insoluble discharge products of NaO$_2$ or Na$_2$O$_2$ deposit onto the air cathode and block the diffusion pathway of oxygen to active sites, leading to the degradation of the performance of Na-air battery. The cycling performance of Na-air battery was found to be dependent on discharge products. Na-air battery showed rather good reversibility of more than 50 cycles and extremely poor reversibility of less than 10 cycles when NaO$_2$ and Na$_2$O$_2$ were formed as discharge product, respectively. It still remains a challenge to seek for highly efficient electrocatalysts for the improvement of cycling performance of Na-air battery. Recently, LiI dissolved in organic electrolytes as catalyst for lithium-air battery was used to dissociate the discharge product of Li$_2$O$_2$, in which I$_3^-$ or I$_2$ formed at the electrode surface could chemically react with Li$_2$O$_2$ to produce Li$^+$ and O$_2$ gas during the charge process [13-14]. These findings have demonstrated that LiI as a redox mediator can effectively enhance the cycling performance of Li-air battery. Enlightened by these works, an attempt was made to investigate the electrochemical cycling performance of sodium-air battery by using NaI as a dissolved catalyst. Here, we introduce a new soluble NaI catalyst for Na-air battery for the first time, which exhibits a long-life cycling performance of up to 150 cycles with a high capacity of 1000 mAh g^{-1}.

The galvanostatic cycling of Na-air cells were performed with the CNT/Ni air cathode (S1) at room temperature. Figure 1(a) shows the initial discharge-charge profiles of the CNT/Ni air electrode using the liquid electrolytes without and with the addition of 0.001 M NaI, respectively. Na-air battery using the liquid electrolytes with the addition of NaI is charged at the depth of discharge (DOD) with a capacity cut-off, while the battery using pristine electrolyte is charged at a fixed voltage of 3.8 V. The data of pure carbon cloth were also included for comparison.

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It can be observed that both discharge and charge capacities of CNT/Ni in the pristine electrolyte are higher than those of pure carbon in the pristine electrolyte when their masses are the same, indicating a higher electrochemical activity of CNT/Ni air electrode than that of carbon cloth electrode. This higher electrochemical activity can be attributed to a larger surface area and higher catalytic activity of CNT attached to the Ni foam [15]. The discharge plateaus of both CNT/Ni and carbon cloth electrodes are at about 2.2 V, which is close to the theoretical value of 2.33 V when Na$_2$O$_2$ is formed as discharge product. Although the initial discharge curve of the CNT/Ni electrode in the pristine electrolyte is similar as that in NaI-containing electrolyte, the charge curve distinctly shifts to lower voltage in NaI-containing electrolyte. The first charge process of the CNT/Ni electrode consists of one shorter plateau at 2.3 V and one longer plateau at 3.2 V vs. Na$^+$/Na. The voltage gap between charge and discharge plateaus in NaI-containing electrolyte is far less than that in the pristine electrolyte. Apparently the electrochemical activity of CNT/Ni electrode in the NaI-containing electrolyte exceeds that in the pristine electrolyte.

Na-air battery was characterized by low DOD (limited to a capacity of 1000 mAhg^{-1}) and the discharge/charge profiles were shown in Figure 1(b)-1(d) and Figure S1 with various concentrations of NaI-containing electrolytes. It can be seen that the discharge and charge polarizations of these cells increase with the cycle numbers, and their cycling performances are strongly dependent on the dissolved concentration of NaI in the electrolyte. Obviously, the discharge and charge process of Na-air battery in 0.05 M NaI-containing electrolyte is highly reversible and stable for up to 150 cycles, which is superior to those of Na-air cells reported previously when either Na$_2$O$_2$ or NaO$_2$ was formed as discharge products as compared in Table S1. It is not sure whether the optimal concentration of NaI is 0.05 M for Na-air battery, which needs further investigation. When an extra certain amount (0.05 M) of NaI was added into the broken battery, whose discharge voltage fell to 1.9 V after 150 cycles, the cycling capability and capacity, discharge/charge voltage platform, and terminal discharge voltage could be fully recovered to the level of a new battery. This phenomenon indicated that the deterioration of the electrochemical performance of Na-air battery should be related to the iodine loss due to the volatilization of iodine in the two-electrode cell during cycling process, which can be confirmed by UV Spectrophotometry (Figure S2). The development of a reliably stable air electrode is indispensable for long-life Na-air battery.
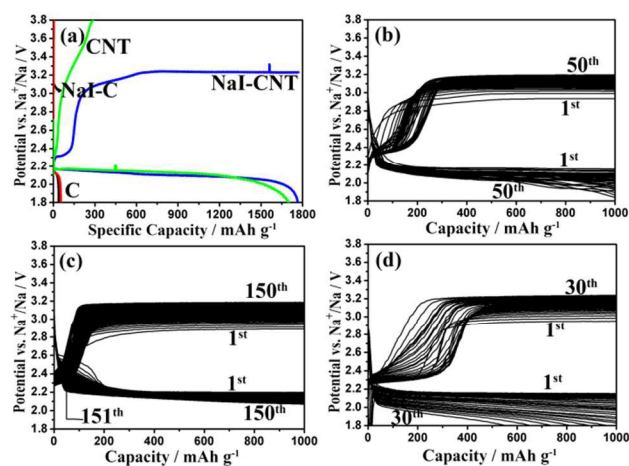
Figure1 (a) Initial discharge-charge profiles of pure carbon cloth and CNT/Ni air electrodes obtained by using liquid electrolytes without and with the addition of 0.001 M NaI, respectively, at the current density of 0.05 mA/cm^2. Cyclic performance of CNT/Ni electrodes using (b) 0.001 M, (c) 0.05 M, (d) 0.10 M NaI-containing electrolytes (the capacity was limited to 1000 mAhg^{-1}) at the current density of 500 mA g^{-1},respectively.

To obtain further insight on the reversible electrochemical reaction mechanism of this cell, the morphology and structure of air electrodes before and after the initial discharge and charge processes were characterized and compared by using *ex situ* TEM and SAED techniques. Na-air battery in 0.05M NaI-containing electrolyte was first discharged to 1.8 V and then charged to 3.3 V at a constant current of 100 mAg^{-1}. Figure 2(a) shows the typical TEM images of the air electrode, in which CNT with a diameter of about 30 nm (the insert of Figure 2(a)) was observed. SAED pattern of the pristine electrode material shown in Figure 2(b) consists of one brighter and one darker ring, both of which could be indexed to CNT. The HRTEM image shows that an ultra-thin film of the product was attached on CNT (labeled by the white arrow shown in Figure 2(c)), and the crystallite s with clear and coherent stripes are observed in enlarged HRTEM images as shown in the insert of Figure 2(c). The corresponding SAED pattern exhibits four clear concentric rings, indicating the nanosized polycrystalline nature of the discharge product (Figure 2(d)). All diffraction d-spacings in the SAED pattern can be well indexed to hexagonal Na$_2$O$_2$ (JCPDS Card No.74-111). This result indicates that nanocrystalline Na$_2$O$_2$ is formed when the cell is discharged to 1.8 V. The same discharge product of Na$_2$O$_2$ could be found in Na-air batteries with various concentrations of NaI-containing electrolyte (Figure S3). The morphology of Na$_2$O$_2$ film attached on the surface of CNT here is similar to the sheet-like Na$_2$O$_2$ reported previously [11], indicating a preferred growth orientation of Na$_2$O$_2$ during discharge process. However, this morphology is different from the cubic shape of NaO$_2$ forming on air electrodes[1-4,6]. These results imply that the morphologies of discharge products should be related to their compositions. Upon charging, Na$_2$O$_2$ is completely removed from the CNT electrode as shown in Figure 2(e), indicating a high reversibility of the air electrode. The diffraction patterns in Figure 2(f) also confirm the absence of Na$_2$O$_2$ after charging.
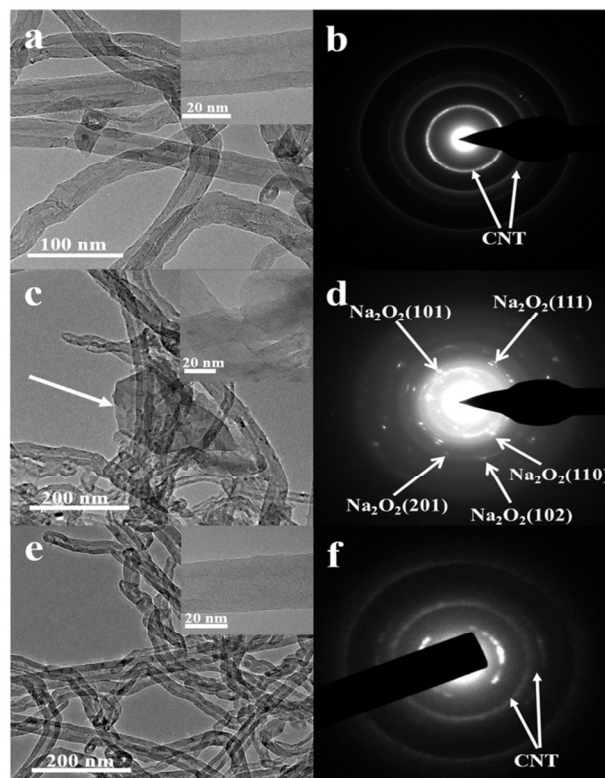

Figure 2 High resolution TEM images of air electrode: (a) before and (c) after initially discharging the cell to 1.8V; (e) after initially charging the cell to 3.3V, and (b), (d) and (f) their corresponding SAED patterns, respectively.

In order to further confirm the composition of the discharge product on the air electrode, the *ex situ* Raman measurements were performed. Figure 3 shows Raman spectra of the pristine air electrode, the electrode after being discharged to 1.8 V and charged to 3.3 V, respectively. The scanning range for Raman measurements was from 500 to 1200 cm^{-1}. Two well-resolved peaks centered at 1350 cm^{-1} and 1580 cm^{-1} from CNT for all air electrodes were not shown here. Interestingly, the new peak appearing at around 730 cm^{-1} can be assigned to the O-O stretch in Na$_2$O$_2$ which is consistent with the standard spectra of sodium peroxide [1]. This data confirms the conversion reaction of oxygen absorbed on the surface of CNT with sodium to form a new product of Na$_2$O$_2$ after the cell is discharged to 1.8 V, which is consistent with TEM and SAED results. Upon charging, sodium peroxide is gradually extracted from air electrode. As a result, the well-resolved peak at 730 cm^{-1} disappears, indicating the decomposition of Na$_2$O$_2$ during charge process.

Based on TEM, SAED and Raman results, the discharge-charge reaction mechanism in Na-air battery with the NaI catalyst is similar to that in Li-air cell with LiI catalyst [13-14]. The following reaction steps are proposed:

At sodium electrode side during the discharge process:
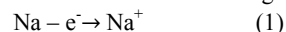
$$Na - e^- \rightarrow Na^+ \qquad (1)$$

At air electrode side during the discharge process:

$$2Na^+ + O_2 + 2e^- \rightarrow Na_2O_2 \quad (2)$$
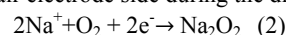
At air electrode side during the charge process:

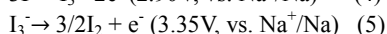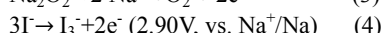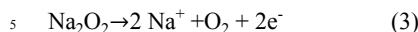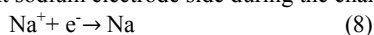**Figure2** Ex situ high resolution TEM images of air
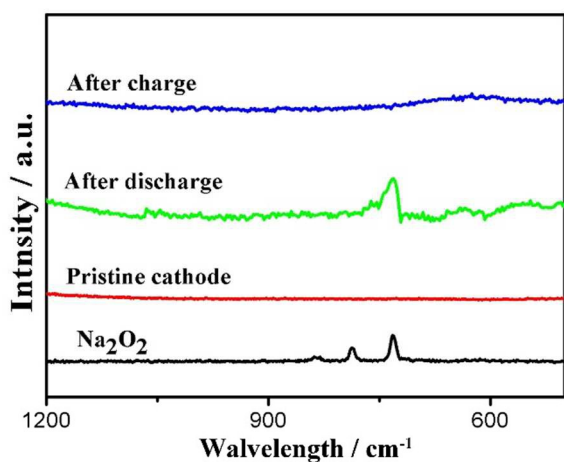
Figure3 Raman spectra of the pristine air electrode and electrodes after being discharged to 1.8V and charged to 3.3V, respectively.

$$Na_2O_2 \rightarrow 2\,Na^+ + O_2 + 2e^- \qquad (3)$$
$$3I^- \rightarrow I_3^- + 2e^- \;(2.90V,\,vs.\,Na^+/Na) \qquad (4)$$
$$I_3^- \rightarrow 3/2 I_2 + e^- \;(3.35V,\,vs.\,Na^+/Na) \quad (5)$$
$$I_3^- + Na_2O_2 \rightarrow 2Na^+ + O_2 + 3I^- \qquad (6)$$
$$I_2 + Na_2O_2 \rightarrow 2Na^+ + O_2 + 2I^- + 2e^- \quad (7)$$
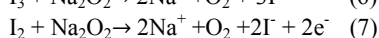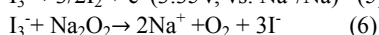
At sodium electrode side during the charge process:
$$Na^+ + e^- \rightarrow Na \qquad (8)$$

As expressed by equations (1) and (2), Na ions will react with oxygen enriched at the surface of the air electrode to form Na_2O_2 during discharge process. The discharge curves exhibit a feature of Na-air battery with the discharge plateau at 2.2 V. However, during charge process, I^- generated from the dissolution of NaI diffuses through DME liquid electrolyte and oxidizes directly at air electrode surface to produce I_3^- or I_2. These oxidized products (I_3^- or I_2) will spontaneously react with Na_2O_2 formed during discharge process to re-generate NaI and release O_2 at air electrode side. In these reactions, NaI dissolved in the electrolyte can freely access to the surface of air electrode, and act as an electron-hole transfer agent between the air electrode and the discharge product of Na_2O_2. The charging voltage plateau at 3.2V might be attributed to the oxidation reaction of active iodine anions, in which the oxidation potentials of I_3^-/I^- and I_2/I_3^- theoretically appear at less than 3.35 V vs. Na^+/Na. This can explain the average charge voltage plateau of 3.2 V as shown in Figure 1. The lower plateau at 2.3 V of the initial charge curve in Figure 1 might be associated with the electrochemical decomposition of Na_2O_2 (equ.(3)). Thus, the sophisticated charge routes should mainly include the electrochemical oxidation of I^- anions (equs. (4) and (5)) and parasitic chemical reaction of I_3^- or I_2 with discharge product (equs. (6) and (7)). Apparently, this reaction mechanism is totally different from previous classical Na-air cells, in which the decomposition of discharge products such as Na_2O_2 was electrochemically driven by carbon or other solid catalysts [7-12]. It should be reasonably assumed that the lower charging potential is most likely related to the electrochemistry of iodine instead of oxides. Although this charge potential at around 3.2 V is much higher than that (<2.5V) in Na-air batteries with the stable NaO_2 as discharge product[1-4,6], the outstanding cycling performance of Na-air batteries with Na_2O_2 as discharge product should probably be attributed to the coordination between two parallel electrochemistry reactions of iodine and chemical reaction of Na_2O_2 with iodine. The comprehensive understanding of this improvement is still under investigation in our group. This soluble catalyst provides a new way to improve the electrochemical performance of Na-air battery.

The effect of an additionally dissolved compound of NaI into the DME electrolyte on the electrochemical performance of Na-air battery was reported. The electrochemistry of iodine instead of oxides should be responsible for the low charging potential of Na-air battery. Na-air battery using the NaI-containing electrolyte showed the outstanding cycling performance over 150 cycles at a limited capacity of 1000 $mAhg^{-1}$ when Na_2O_2 is formed as discharge product.

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