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Toward a Sodium−"Air" Battery: Revealing the Critical Role of Humidity

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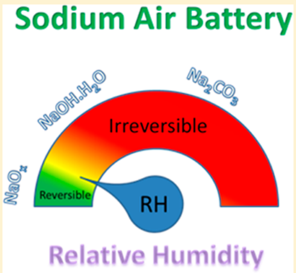
Supporting Information

ABSTRACT: Room temperature sodium−air batteries have a similar design and concept as lithium−air batteries. Using ambient air instead of pure oxygen as oxygen source is challenging because the minor components in air could lead to various side reactions and influence the electrochemical reaction route. Although water is an innegligible component in air, its impact on Li− and Na−air batteries is often underestimated. In this study, the electrochemical behavior of Na−air batteries under different relative humidity (RH) has been systemically investigated by galvanic cycling and cyclic voltammetry tests, as well as the identification of corresponding discharge products by physical characterizations such as XRD, FT-IR, and SEM. The reaction mechanisms of Na−air batteries under humid conditions are revealed and discussed. Na−air batteries suffer from more severe impact from the water content in air than Li−air batteries. NaOH and its derivatives are found to form and are proven to be fatal to the cells under humid ambience. Understanding the reaction mechanisms occurred in sodium air batteries under dry and humid ambient is critical to design and develop sodium−air batteries of high performance and long durability.



1. INTRODUCTION

As a newly developed member of metal−air batteries, sodium−air batteries (SABs) are attracting increasing research interest due to their high theoretical energy density and environmentally benign characteristics.[1−4] The concept of SABs are similar to lithium−air batteries (LABs), which have been widely studied over the last decades.[5−8] SABs and LABs are comprised of an air electrode for oxygen reduction and solid-state discharge product formation and accommodation, a separator acting as a barrier, and metal Na or Li as an anode. Despite their similar battery concept and design, different types of discharge products have been found in LABs and SABs. Li_2O_2 has been detected as the major discharge product of LABs,[5−8] while NaO_2,[9−12] Na_2O_2 and/or their derivatives,[13−20] and/or Na_2CO_3[21,22] have been reported as the discharge products in different studies on SABs as well. This distinction between the SABs and LABs is due to the different thermodynamic stabilities of LiO_2 and NaO_2, despite the similar alkali element characteristics of Li and Na. It is now widely accepted that the reaction mechanisms in LABs involve two steps of O_2/O_2^- and $LiO_2 \rightarrow Li_2O_2$.[5,8] However, LiO_2 is highly unstable under room temperature and normal pressure, while NaO_2 has shown to be more stable under certain conditions.[12,23] Therefore, both NaO_2 and/or Na_2O_2 can be formed as the discharge products in SABs. The formation of certain types of discharge product(s) is related to a series of factors, such as grain size,[23] working temperature,[24] O_2 concentration under flowing or static condition,[25] and/or charge/discharge current density.[18] Interestingly, the charge overpotential of SABs is much lower than that of LABs when NaO_2 is the discharge product.[9,25,26] Thus, it is of great interest to develop this novel energy conversion system. However, the current understanding of SABs is still insufficient and requires further fundamental studies.

A significant challenge for both LABs and SABs is moving from Li−"O_2" or Na−"O_2" batteries to Li−"air" and Na−"air" batteries, i.e., using ambient air instead of pure oxygen. The minor components in air other than oxygen and nitrogen could lead to various side reactions, which can possibly influence the electrochemical reaction route and therefore be fatal to the performance of the metal air batteries. For example, the impact of carbon dioxide (CO_2) on lithium-[27,28] and sodium−air batteries[29,30] has been investigated by different groups with Li_2CO_3 or Na_2CO_3 forming, respectively. Further, as an non-negligible component in air, water (H_2O) is another important factor deserving serious consideration for LABs and SABs. The concentration of H_2O in air is generally expressed by relative humidity (RH), which is calculated by the ratio of the actual water vapor pressure to the saturation water vapor pressure at the same temperature. Although one may expect that water will be devastating for Li/Na−air batteries due to its reactivity toward Li/Na superoxides or peroxides, the role of humidity has been found to be much more unexpected and sophisticated in Li−air batteries. Organic ether-based electrolytes currently used in Li− and Na−air batteries have been shown to be relatively more stable against minor amount of water than carbonate electrolytes commonly used in Li-ion batteries or early studies of Li−air batteries, making the influence of water toward the Li−air batteries more subtle. Meini et al.,[31,32] Guo

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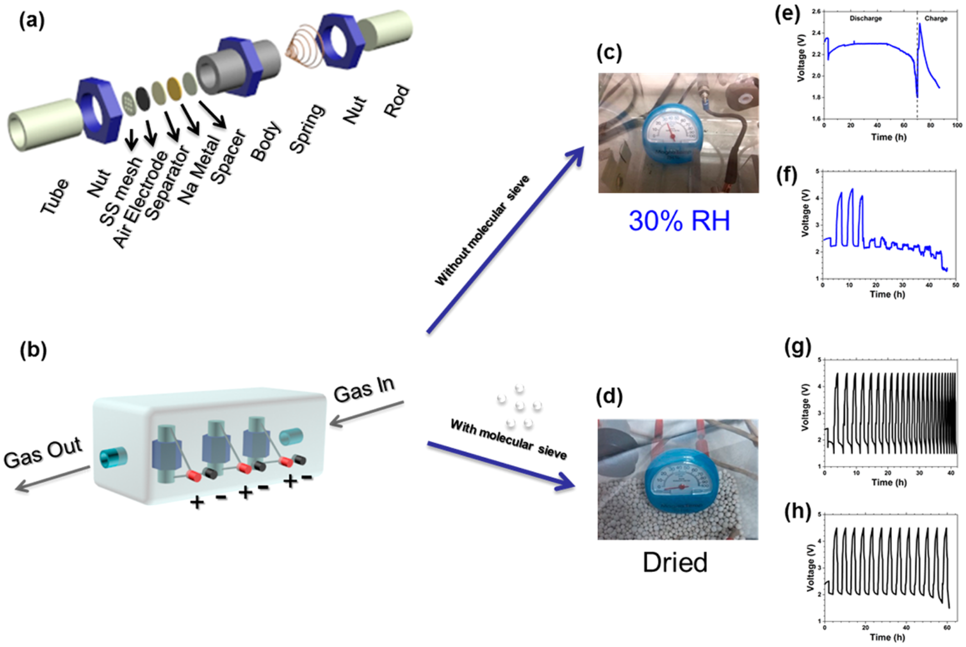

Figure 1. Schematic diagram of (a) a typical Swagelok-type sodium−air cell and (b) container for battery testing; optical pictures of humid meter during battery testing under (c) 30% RH and (d) dry ambience; charge and discharge curves of sodium−air batteries at 100 mA/g_{carbon} under 30% RH with (e) cutoff voltage between 1.8 and 4.5 V at 100 mA/g_{carbon} and (f) cutoff capacities of 300 mAh/g_{carbon} at 150 mA/g_{carbon}; charge and discharge curves of sodium−air batteries under air-dried with molecular sieves with (g) cutoff voltage between 1.5 and 4.5 V at 200 mA/g_{carbon} and (h) cutoff capacities of 300 mAh/g_{carbon} at 150 mA/g_{carbon}.

et al.,[33] Cho et al.,[34] and Schwenke et al.[35] have addressed the role of moisture in the electrochemical behavior in LABs, respectively. It is commonly found that the discharge capacities of the cells significantly increased after water was introduced. Consequently, LiOH was observed as a major side product rather than Li_2O_2 under high RH.[33] More interestingly, it is recently reported that the formation and growth of large Li_2O_2 toroids can be even promoted by adding water to electrolytes.[35,36] It is reported that no LiOH was detected in cathodes discharged in electrolytes with up to 1% of water.[35] Additionally, Meini et al. showed that the presence of water did not change the charge capacity of the prefilled Li_2O_2/carbon electrodes, but significantly reduced their activation peak potentials when the Li metal anode was carefully protected.[32] In contrast, Cho et al. reported that unprotected Li metal anode was highly vulnerable to water contamination and lead to limited cycling lives.[34] These studies have throughout investigated the severe impact and complex reaction mechanism of water in Li−air batteries. Nevertheless, the impact of water content in air on SABs has not been fully revealed.

In this work, we systematically investigated the influence of relative humidity on the electrochemical behavior and reaction mechanism of SABs for the first time. The SABs were tested under dry and wet ambience using air electrodes made from commercial carbon nanotubes (CNTs). The electrochemical and chemical reaction mechanisms were investigated by charge and discharge and cyclic voltammetry measurements combining with X-ray diffraction and scanning electron microscopy characterizations. The critical role of humidity effect in the performance is revealed.

2. EXPERIMENTAL METHODS

2.1. Preparation of CNT Air Electrodes. CNT air electrodes were fabricated by mixing CNT powder with PVDF binder in a ratio of 8 to 2, followed by dispersing via sonication, and finally casted on a commercial separator film substrate (Celgard 3501). The total masses of CNT + PVDF loaded on air electrodes ranged between 0.4 and 0.1 mg, and their thicknesses are approximately 5−7 μm (Figure S1, Supporting Information).

2.2. Electrochemical Measurements. The Swagelok-type Na−air cells were assembled from a metallic sodium foil anode, polypropylene separator (Celgard 3501), and CNT air electrode, as well as a stainless steel mesh current collector. The electrolyte was comprised of 0.5 M sodium triflate ($NaSO_3CF_3$, Aldrich) dissolved in diethylene glycol diethyl ether (DEGDME, Aldrich). The DEGDME solvent was dried with molecular sieves (4 Å, Aldrich) for at least one month before use.

The discharge/charge characteristics were performed using an Arbin BT-2000 battery station in a sealed box filled with a 1.0 atm dry or humid atmosphere at room temperature (298 K). Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) measurements were carried out with a multi potentiostats (VMP3, Biologic).

2.3. Physical Characterizations. The morphologies of the discharge products were observed by a Hitachi S-4800 field-emission scanning electron microscope (SEM). Their compositions are determined by X-ray diffraction (XRD) measurements, which were recorded using a Bruker D8 Advance (Cu Kα source, 40 kV, 40 mA) spectrometer. Fourier transform infrared (FT-IR) spectra were recorded using a Nicolet 380 (Thermo Scientific).

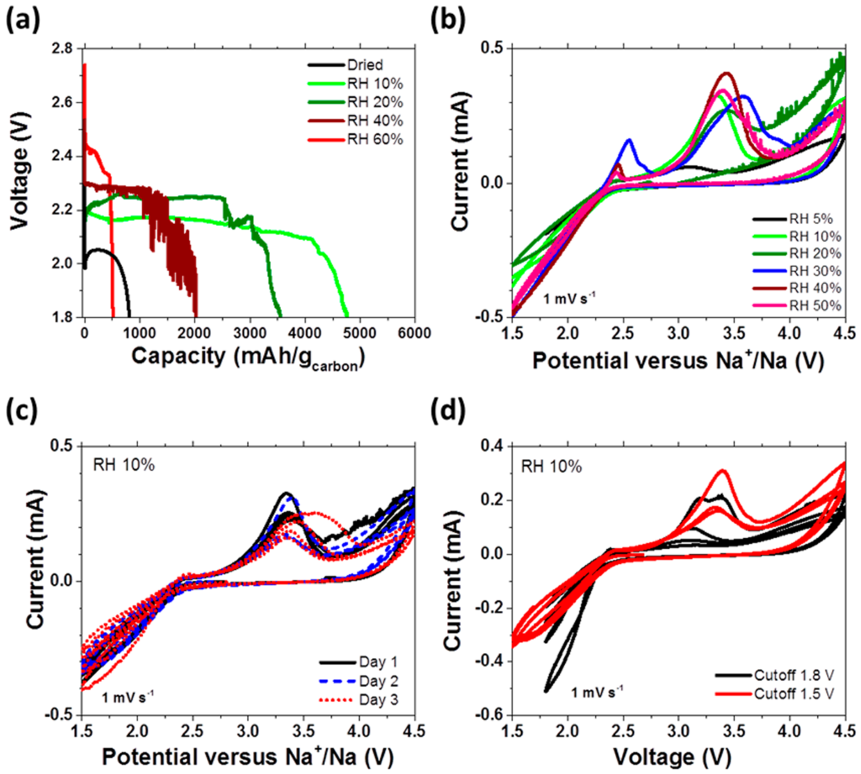

Figure 2. (a) First discharge curves of sodium−air batteries with CNT electrode under dry and humid air ambience with different RH% value; (b) first cycle CV curves of the sodium−air batteries with CNT air electrodes between 1.5 and 4.5 V under humid air with different RH% value; (c) initial three cycle CV curves of the sodium−air batteries with CNT air electrodes between 1.5 and 4.5 V under humid air with 10% RH tested in three individual days; (d) first three cycle CV curves of the sodium−air batteries with CNT air electrodes under humid air with 10% RH between 1.5 and 4.5 V and between 1.8 and 4.5 V.

3. RESULTS AND DISCUSSION

Up to now, various designs of SABs have been used in previous studies, e.g. Giessen cell[12] and H-shape tube.[13] In this study, we used a Swagelok-type design to assemble sodium air battery, which is similar as those adopted in LABs.[37,38] As depicted in Figure 1(a), the Swagelok-type SABs are composed of plastic and metal Swagelok units combining with a stainless steel mesh current collector, an air electrode, a separator, and a piece of sodium metal as the anode. The side of the air electrode was exposed to the air, while the opposite side was sealed. Electrolyte plays a very important role in Li-/Na−air batteries. On one hand, ether-based electrolyte is known to be more stable for alkali metal batteries.[4,5,39] On the other hand, electrolyte salts may also decompose due to their reactions with O_2^{-}·.[40,41] 0.5 M $NaSO_3CF_3$ in DEGDME is chosen as electrolyte in this study, which has been widely adopted in the study of Na−air batteries.[9,12,17,18,20] It is worthy to note that micrometer sized NaO_2 was reported to form in $Na-O_2$ battery with this electrolyte.[9] Thus, it is reasonable to assume that this composition of electrolyte is relatively stable against superoxide and therefore suitable to demonstrate the influence of RH on Na−air batteries. Meanwhile, considering it is also the most common choice for Na−air batteries, using this certain electrolyte will also be helpful to contribute better understanding to practical usage of Na−air batteries. The CV measurement on Na−air batteries with CNT air electrode was carried out in an Ar-filled glovebox and the curves are shown in Figure S2, where no obvious redox peaks can be observed. The CV curves under Ar were stable and well overlapped during several cycles, indicating the stability of the electrolyte in this study. The SABs were tested in a homemade plastic container with an inlet and outlet for gas (Figure 1b). We used mechanical humidity meters to measure the relative humidity (RH) in the air at room temperature (25 °C). A typical RH of 30% was observed for ambient air without any drying (Figure 1c). For comparison, molecular sieves were placed in the testing container to achieve a dry air environment (Figure 1d).

As a conventional and commercial material, CNTs have been widely used as air electrodes for SABs in previous studies by different groups.[20,25,42−44] We have also previously examined the performance of CNT air electrodes under pure oxygen for SAB,[20] and found that it exhibited a similar electrochemical performance as other studies. Surprisingly, the Na−air cells tested in wet and dry air exhibited considerably different electrochemical performances in this study. As shown in Figure 1e, the cell cycled in 30% RH displayed a long first discharge plateau for around 70 h at 50 mA/g. However, the cell was not rechargeable. After the cell was first charged to around 2.5 V, its voltage started to decrease and the cell rapidly decayed. This phenomenon was repeatedly witnessed in the charge and discharge curves of the SABs under wet ambience in this study. Even further, charging and discharging with a limited cutoff capacity of 300 mAh/g revealed that the reversible charge and discharge processes can only be achieved in the first several cycles (Figure 1f). After three cycles, the charge and discharge curves of the Na−air cell appeared to be noisy, and the cell could not be charged over 2.5 V. In contrast, the Na−air cell in dried air exhibited much longer cycling lives but with lower capacities. When discharged and charged between 1.5 and 4.5 V, a typical Na−air cell can be cycled for around 20 times

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(Figure 1g), while another cell cycled under dry air with a limited cutoff capacity of 300 mAh/g exhibited a cycle life of 14 cycles (Figure 1h). Interestingly, Guo et al. reported that in a wet ambience with the RH of 15% and 50%, the cycling lives of Li−air cells were limited to about three cycles under full charge and discharge cycling between 2.0 and 4.5 V, but could reach 30−50 cycles at a limited cutoff capacities of 1000 mAh/g.[33] Schwenke et al. also reported the Li−air batteries with 1% water content could be rechargeable for around 10 cycles.[35] This comparison implies that the SABs are more sensitive to the water content in air. Therefore, it can be concluded that maintaining a dry condition is even more critical to enable long-term cycling of SABs than LABs.

To further reveal the impact of relative humidity on the electrochemical performance of SABs, Na−air cells were discharged under different humidity conditions with RH ranging from 10% to 60% at the same current density of 100 mA/g. The first discharge curves are shown in Figure 2a. The discharge capacities of the cells under humid conditions ranged from 4747, 3547, and 2016 mAh/g with the RH of 10%, 20%, and 40%, which are about 5, 3.5, and 2 times higher than the cell under dry air (781 mAh/g), respectively. The cell discharged in an environment with a RH of 60% failed with a sharp voltage drop before fully discharging and displayed a lower capacity of 520 mAh/g. The increased capacities of the SABs under humid conditions over those cycled under dry air are consistent with those reported in LABs. Meini et al. reported that the discharge capacities of a LAB with a leakage of 1000 ppm water were 2.8 times of that of a water-free cell.[31] Guo et al. found the discharge capacities of lithium air cells under RH of 15% and 50% are about twice of that under pure/dry oxygen at 100 mA/g.[33] On the other hand, it should be noted that the plateau voltage of the discharge curves increased with the increase of water content in air for all the Na−air cells. Similar trend regarding to the increased discharge voltage as increasing humidity were also witnessed in the study of LABs and believed to be related to the formation of LiOH, which has shown a 40 mV higher redox potential than the cells producing Li_2O_2.[31] Meanwhile, the shapes of the discharge curves of the Na−air cells discharged with the RH of 20%, 40% and 60% appeared to be noisy after certain states of discharge. These evidence strongly imply that the electrochemistry and chemistry of SABs can be altered with the existence of water. Hydroxides may have formed as discharge products under humid condition.

In order to verify the above assumption, we carried out cyclic voltammetry (CV) measurements under the ambient air with different RHs. As shown in Figure 2b, the CV curves of the cells exhibited totally different characteristics. The shapes of cathodic peaks in the CVs are similar, however the cathodic currents gradually increased along with the increasing RH values. Meanwhile, the shapes and positions of the corresponding anodic peaks differed under different RHs. At a very low RH of 5%, a single anodic peak located at 3.10 V is observed, which is consistent with the CVs of the Na−air cell with a graphene air electrode producing Na_2O_2 as the discharge product.[17] However, when the RH increased to 10% and 20%, the corresponding single anodic peak shifted to 3.35 and 3.41 V, respectively, and the anodic currents significantly increased as well. When the RH was further increased to 30%, four strong anodic current peaks appeared at 2.55, 2.67, 3.58, and 3.89 V. For the cells under RH of 40% and 50%, two groups of anodic peaks centered at around 2.44 and 3.41 V were witnessed. When the RH was further increased, abnormal CV curves were achieved (Figure S1). In spite of their similar cathodic current response, extremely large anodic currents are observed around 2.6 and 3.5 V under 60% and 70% RH, which should not be contributed by the decomposition of the electrochemically reduced products, implying the side chemical reactions. The CV measurements indicate that side chemical reactions occur in the SABs even under low humidity environment. Zhao et al. reported that the potential of electrochemical decomposition of $Na_2O_2{\cdot}2H_2O$ occurs around 2.4 V, following the route $Na_2O_2{\cdot}2H_2O \rightarrow 2NaOH + H_2O + O_2$.[25] In addition, the theoretical thermodynamic potentials of reactions $2NaOH \rightarrow 2Na^+ + 2e + H_2O + {}^1/_2O_2$ with solid or aqueous NaOH are calculated to be 2.71 and 3.11 V.[25] The formation of $Na_2O_2{\cdot}2H_2O$ can be attributed to the reaction between the discharge product Na_2O_2 with H_2O in air,[25] or decomposition of electrolyte.[16] Thus, it might be implied that hydrated sodium peroxide and sodium hydroxide forms in humid conditions. The anodic peaks located ranging around 2.4 and 2.5 V can be assigned to the decomposition of $Na_2O_2{\cdot}2H_2O$ or solid state NaOH, while the peaks around 3.4 and 3.5 V may be related to the decomposition of aqueous NaOH. As the RH increases to a medium range between 30% and 50%, a liquid water phase may have formed from either the absorption of the gas phase H_2O in air or as an electrochemical decomposition of the solid state NaOH or $Na_2O_2{\cdot}2H_2O$. Solid state NaOH first decomposed at a low potential. Afterward, the solid NaOH product can dissolve in the liquid water and decompose at higher potential. Under a highly humid ambience (60%−70%), the absorption of H_2O from air severely influenced the SABs, which not only alters the electrochemical reaction mechanism but also may penetrate the cell and directly chemically react with metallic Na anode following the reaction $2Na + 2H_2O \rightarrow 2NaOH + O_2$. Similar reactions between metal Li and water from air has been reported in Li−air cells.[34] This reaction resulted in the failure of the cell and corresponded to the large anodic current around 3.5 V in their CVs. The further identification of the discharge products by physical characterizations will be discussed in the following part of this study. We have also carried out the CV measurements under air with 10% RH in three different days. It can be seen from Figure 2c that the cells have exhibited similar CV curves, indicating the similar reaction mechanism under the same RH. Interestingly, at 10% RH the CV curves of the cells are relatively reversible and stable between 1.5 and 4.5 V. However, when the cutoff voltage changed to between 1.8 and 4.5 V, the CV curves of the cell quickly decayed (Figure 2d). This result also implies an irreversible process occurred first at the higher discharge voltage, which is consistent with the higher potential of the electrochemical formation of NaOH than NaO_2 or Na_2O_2 as discussed above.

To achieve direct evidence on the reaction route and mechanism of the SABs under dry and humid air, we disassembled the cells cycled in dry and wet air, respectively, for further characterization. From their optical pictures (Figure 3a), it can be clearly observed that the air electrode and current collector from the dry cell are clean with a well maintained shape. However, the CNTs in the air electrode discharge from the humid air cell were detached from the original substrate and clipped to the current collector. The color of the substrate separator also changed, implying the possible contamination from side reaction products. The difference between the morphologies of the discharge products of the two samples are revealed by their SEM images. As for the electrode from the cell

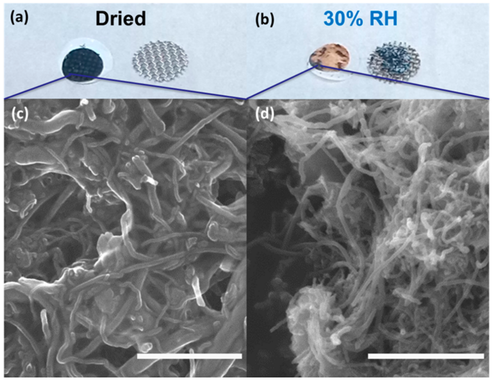

Figure 3. (a, b) Optical and (c, d) SEM pictures of cycled CNT air electrodes under dry and humid (30% RH) ambience; the scale bars stand for 1 μm.

in dry air, the discharge products accumulated on the surface of the CNTs. Nevertheless, the discharge product of the electrode with RH 30% seems to be encased by the CNTs, while the surfaces of CNTs are smooth and clean. This evidence is consistent with the previously observed electrochemical behavior of the presented SABs in this study. It is known that the distribution of discharge products in alkali metal−air batteries can be not uniform,[45] while the pore structure of air electrodes plays an important role in their electrochemical performance and discharge capacities.[46−48] When the solid state product aggregates on the surface of air electrode in a dry ambience, further oxygen gas diffusion is blocked and results in a relatively low capacity of the cell. Meanwhile, the rechargeability of these batteries also relies on the amount of the pores which are filled with decomposition products. In the case of higher content of H_2O in the air, the discharge products can absorb and react with H_2O and therefore transform to another phase with a different morphology. Thus, the oxygen reduction processes can be promoted in the SABs under relatively low RH condition, which is similar to the concept of Li−water fuel batteries proposed by Wang and Zhou.[49]

X-ray diffraction (XRD) analysis was carried out to determine the composition of the discharge products under dry and wet air with RH of 10%, 30% and 60%, respectively. A discharged electrode in dried air or 10% RH was directly used for XRD measurement. For the cells discharged in humid conditions higher than 30% RH, due to the fact that the discharge products and most of the CNTs had been transferred to the current collector, an air electrode attached to the current collector was used together as a whole part for XRD analysis. As shown in Figure 3(b), it is clear that NaO_2 and Na_2O_2 are both detected as the discharge product under dry air, which is consistent with the previous work from our group where pure oxygen was used.[17] When the RH increased to 10%, two weak diffraction peaks assigned to NaOH in addition to the Na_2O_2 peaks appeared in its XRD pattern. However, all the diffraction peaks except for two from current collector can be assigned to $NaOH.H_2O$ for the XRD pattern of the discharged electrode with 30% RH. Only peaks from the current collector can be observed in the XRD pattern of the discharged electrode with 60% RH, indicating that the products are noncrystallized. The infrared (IR) spectra of the discharge products also support the formation of NaOH-like species under humid air with RH of 30%, while more sodium carbonate Na_2CO_3 content may exist in the discharge products in 60% RH (Figure 4(b)). These results provide further evidence that hydroxides formed in the Na−air cells in humid conditions. The evolution of the discharge products of SABs versus RH are summarized in Figure 4c combining the XRD and FT-IR evidence.

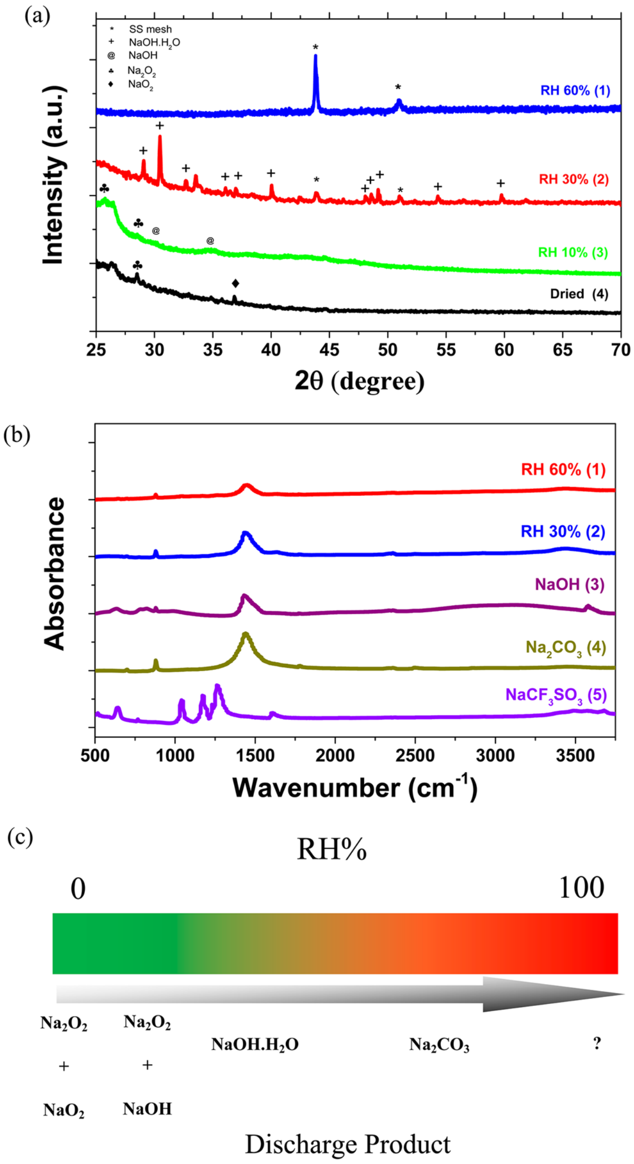

Figure 4. (a) XRD patterns of discharged CNT air electrodes under (1) 60% RH, (2) 30% RH, (3) 10% RH, and (4) dried ambience; (b) FT-IR spectra of the discharged electrodes under humid air with RH of (1) 60% and (2) 30%; FT-IR spectra of standards (3) NaOH, (4) Na_2CO_3, and (5) $NaCF_3SO_3$ (electrolyte salt) are also presented for comparison; (c) schematic diagram of the evolution of discharge product of sodium−air batteries versus RH%.

Interestingly, although LiOH has been also considered and widely detected as a side product in LABs,[50,51] its impact on the cycling performance of LABs was not as fatal as that of NaOH in SABs. It is reported that even in the air with RH of 50%, the XRD pattern displayed the coexistence of LiOH, Li_2CO_3 and Li_2O_2.[33] However, Na_2O_2 could not be detected in the SABs cycled under a RH of above 30% in this study. This distinction should be assigned to the chemical property of NaOH, which is prone to deliquescence. Thus, the following reactions may occur:

$$\mathrm{NaOH(s) + H_2O(g) \rightarrow NaOH{\cdot}H_2O(s)} \qquad \text{(chemical)}$$

$$\mathrm{NaOH(s)} + n\mathrm{H_2O(g) \rightarrow NaOH(aq)} + n\mathrm{H_2O(l)} \qquad \text{(chemical)}$$

Meanwhile, during the electrochemical charging process, the hydrated NaOH may also release liquid phase water reaction expressed as

$$\mathrm{4NaOH{\cdot}H_2O(s) \rightarrow 4Na^+(sol.) + 4e + O_2(g) + 6H_2O(l)} \qquad \text{(electrochemical)}$$

When liquid phase water forms, it may either dissolute or react with the discharge product in the cell. Further, it may also reach and react with the metal sodium anode. The possible reactions include:

$$\mathrm{NaOH(s) + H_2O(l) \rightarrow NaOH(aq) + H_2O(l)} \qquad \text{(chemical)}$$

$$\mathrm{2NaO_2(s) + H_2O(g\,or\,l) \rightarrow 2NaOH(s\,or\,aq) + H_2O(l)} \qquad \text{(chemical)}$$

$$\mathrm{Na_2O_2(s) + 2H_2O(g\,or\,l) \rightarrow 2NaOH(s\,or\,aq) + H_2O_2(l)} \qquad \text{(chemical)}$$

$$\mathrm{Na_2O_2(s) + 2H_2O(g) \rightarrow 2Na_2O_2{\cdot}2H_2O(s)} \qquad \text{(chemical)}$$

$$\mathrm{2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)} \qquad \text{(chemical)}$$

$$\mathrm{2Na(s) + 2H_2O(l) \rightarrow 2NaOH(s\,or\,aq) + H_2(g)} \qquad \text{(chemical)}$$

In order to confirm the origin of NaOH and verify the stability of the electrolyte salt ($NaCF_3SO_3$) to water, we carried out an additional experiment: (a) $NaCF_3SO_3$ is exposed in ambient air for 2 weeks (RH ranged in 10–20%) and referred as sample **1**; (b) $NaCF_3SO_3$ is first dissolved in deionized water (Figure S4) and then evaporated in a vacuum oven at 120 °C for 10 h and referred as sample **2**. Afterward, we checked the FT-IR spectra of the above two samples. The results are shown in Figure S5 in the Supporting Information. It can be observed that the FT-IR spectra of both samples **1** and **2** show similar features to the initial $NaCF_3SO_3$, while no absorption peak corresponding to either NaOH or Na_2CO_3 can be observed. These results indicate that $NaCF_3SO_3$ is also stable versus water. Therefore, it can be concluded that NaOH or Na_2CO_3 in discharge products was not resulted from the chemical reaction between the electrolyte and water.

Moreover, from the XRD patterns and FT-IR spectra of the discharge products under different RH% levels, it can be concluded that at relatively low RH% range, NaO_x and/or NaOH and its derivatives were detected as the major component. While under a high RH% of 60%, only Na_2CO_3 was detectable. These evidence indicate that the formation of Na_2CO_3 was dominating under higher RH%. The reason to this phenomenon should be attributed to the difference of the kinetics of the reaction between the initial discharge products and CO_2 from ambient air. As discussed, liquid phase water may be resulted from the deliquescence of NaOH and absorption from the moisture in high RH% air. Meanwhile, it has been shown that NaOH aqueous solution is a well-known good chemisorbent for CO_2-capture to form Na_2CO_3, but the reaction between solid-state NaOH and CO_2 is very slow:[52]

$$\mathrm{2NaOH(s) + CO_2(g) \rightarrow Na_2CO_3(s) + H_2O(l)} \qquad \text{(slow, chemical)}$$

$$\mathrm{2NaOH(aq) + CO_2(g) \rightarrow Na_2CO_3(aq) + H_2O(l)} \qquad \text{(fast, chemical)}$$

These possible reaction routes are also consistent with the over amounted side products formed on the air electrode after cycled in the wet air with RH of 60% and 70% (Figure S6).

On the basis of the above analysis, it can be inferred that even at relative low humidity level, the chemical and electrochemical reaction mechanisms of SABs can be altered. In order to explain why the water species in air have significant influence on SABs comparing to LABs, the theoretical redox potentials for the possible electrochemical reactions with and without water in SABs are calculated based on the calculation of thermodynamic equation $\Delta G^0 = -nFE^0$ and Nernst equation $E = E^0 + RT/nF \ln(a_{ox}/a_{red})$, where ΔG^0 is the change in Gibbs free energy, n is the number of electrons transferred per mole, F is the Faraday constant (96485 C/mol), E^0 is standard electrode potential, E is theoretical electrode potential (electromotive force), R is gas constant (8.314 J/(K·mol)), T is absolute temperature (K), and a_{ox} and a_{red} are chemical activities for reductant and oxidant, respectively. The saturated water vapor pressure at room temperature (25 °C or 298 K) is 3.1690 kPa. The oxygen partial pressures for pure oxygen and air are simply assumed to be 1 and 0.2 atm (1 atm =101.325 kPa), respectively.

The calculated electromotive forces (EMFs) for the reactions are depicted in Figure 5. The results in regards to the electrochemical Na–O_2 reactions (2.26 V for NaO_2 and 2.33 V for Na_2O_2 under pure oxygen) are consistent with the values calculated in previous reports,[12,13,25] while the corresponding EMFs have a slight difference when changed from pure oxygen to simulated air (20% O_2). However, the EMFs for electrochemical formation of NaOH ($4Na^+ + 4e + 2H_2O(g) + O_2(g) \rightarrow 4\,NaOH(s)$) varied from 2.63 to 2.58 V, assuming that the air's RH ranges from 100% to 1% at 25 °C. It should be noted that this theoretical voltage is actually close to the observed "dead" charging voltage of the cells reported here and consistent with the position of anodic current peaks in the CV curves. This is also consistent with the observed higher discharge voltages of the cells in humid air than those under dry conditions, supporting the involvement of water in the both electrochemical and chemical reactions. This evidence suggests that the failure of the cells is likely related to the release of water during charge cycle. A similar increase in the discharge voltages was also seen in the study on LABs in humid

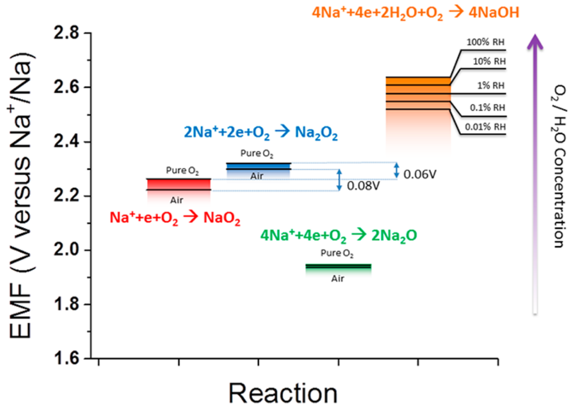

Figure 5. Evolution of theoretical redox potentials of the possible reactions in sodium–air batteries under pure oxygen or dry/humid air.

conditions.[31] In addition, the decomposition voltage of LiOH is predicted to be 4.67−5.02 V according to theoretical calculations,[53] which is even higher than that of Li_2CO_3 (4.38−4.61 V). Considering the fact that in the studies of LABs, the charging voltage cutoff are commonly limited to below 4.5 V, it is therefore reasonable to assume that LiOH phase is hard to decompose and release water to contaminate the LABs. In contrast, it has recently been experimentally proven that the NaOH phase can be decomposed around 3.15 V in SABs.[25] It is also worthy to note that Kang's group recently reported that the decomposition energy barrier for Na_2O_2 and NaO_2 are theoretically calculated to be lower than Li_2O_2.[20] Thus, the difference between the decomposition of sodium and lithium hydroxides may be further explained based on theoretical calculation or subsequent experiments in future.

In this study, in order to achieve general information on the RH effect on Na−air batteries, we started from CNT electrode, which is not catalytic active. Catalysts play very important and rather sophisticated roles in metal−air batteries. They can contribute to improving ORR and OER processes in the metal−air batteries, reducing the overpotential and/or helping to decompose both discharge products and side reaction products.[54−57] Thus, it can be expected that the Na−air batteries will exhibit more complicated reaction routes under wet environment after introducing catalyst layers. Thus, we also tested a SAB under wet conditions using nitrogen-doped carbon nanotubes (NCNTs), which have been reported as functional ORR and OER catalyst for both Li− and Na−air batteries.[20,58,59] One typical discharge and charge curve of NCNT air electrode tested under 30% RH is presented in Figure S6 in Supporting Information. Similar as pristine CNT air electrode, NCNT air electrode discharged in wet ambience also exhibited large but irreversible gravimetric capacities. The voltage of the cell started to drop after a short period of charging. Therefore, it should be concluded that the impact of RH on Na−air batteries is very severe, which need to be addressed prior than exploring better catalysts. Besides, it should be noted that different discharge products have been reported in different studies on Na−air batteries up to now. In this work, we have shown that the discharge product of Na−air batteries can be altered ranging from sodium superoxide and peroxide to hydroxides and carbonates under different RHs, even with the same air electrode composition and cell configuration. We believe that these evidence could be helpful to address the discrepancies in the studies on Na−air batteries and provide a better understanding of the formation mechanism of their discharge products in Na−air batteries.

4. CONCLUSIONS

In summary, the roles of relative humidity in the electrochemical behavior of SABs using CNT air electrodes were investigated in detail. The electrochemical performances of SABs are highly sensitive to the moisture in air. Although the discharge capacities of SABs under humid ambience significantly increased when compared with those of the cells under dry air, the reversible cycling of SABs can be only realized under dry environment. The existence of moisture in air significantly alters the electrochemistry and chemistry of SABs even at relevant low relative humidity. Comparing to LABs, the electrochemical formation/chemical transformation of sodium hydroxide or its hydrated derivatives are much more thermodynamically favored in SABs. When NaOH forms, gas phase water can be absorbed by the air electrode from air and liquid phase water can be released during the cell charging process, causing short-circuit and failure of the cell. Understanding the reaction mechanisms occurring in SABs under dried and wet ambience is critical to design and develop SABs with high performance and long durability

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

SEM images, supplemental CV curves, optical pictures, FT-IR spectra, and charge−discharge curves. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jpcc.5b02673.

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Notes

The authors declare no competing financial interests.

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