

# 3D Printing of Free-Standing "O<sub>2</sub> Breathable" Air Electrodes for High-Capacity and Long-Life Na-O<sub>2</sub> Batteries

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**ABSTRACT:** Superoxide-based Na–O<sub>2</sub> batteries have been considered as some of the most promising candidates for next-generation energy storage systems due to their high theoretical energy density and energy efficiency. However, to fully realize the advantages of Na–O<sub>2</sub> batteries, the underutilization of air electrodes and poor cycling performance caused by limited O<sub>2</sub> transport in the air electrodes must be addressed. In this work, 3D printing of a reduced graphene oxide (rGO)-based air electrode with a hierarchical porous structure was first demonstrated as being "O<sub>2</sub> breathable" for Na–O<sub>2</sub> batteries. The unique cathode structure features noncompetitive and continuous pathways for O<sub>2</sub>, Na<sup>+</sup> ions, and electrons. The macropores provide smooth passages to facilitate O<sub>2</sub> access across the whole electrode, while the micropores between rGO sheets serve as electrolyte reservoirs and accommodate NaO<sub>3</sub>. The



efficiently packed rGO sheets ensure sufficient electronic conductivity within the 3D architecture. Na $-O_2$  batteries using these " $O_2$  breathable" electrodes can achieve a high capacity of 13484.6 mAh g<sup>-1</sup> at 0.2 A g<sup>-1</sup> and a stable cycling performance over 120 cycles with a cutoff capacity of 500 mAh g<sup>-1</sup> at 0.5 A g<sup>-1</sup>. The 3D-printed " $O_2$  breathable" electrodes evidently demonstrate the importance of a refined balance between electronic conductivity and  $O_2$  transport for high-performance Na $-O_2$  batteries.

## INTRODUCTION

The depletion of fossil fuels and undesirable environmental consequences have dramatically promoted an extensive search for new energy storage systems, including Li-S and metal-O<sub>2</sub> batteries.<sup>1-5</sup> Among them, rechargeable Na-O<sub>2</sub> batteries have attracted significant attentions due to their high theoretical energy density, high energy efficiency, and environmental benignity.<sup>6-8</sup> The low cost and abundance of the Na element are additional advantages of the Na-O2 battery system with respect to energy storage for next-generation electric vehicles. However, the practical discharge capacities of Na-O<sub>2</sub> batteries are still far from the theoretical value, and their cycling performance is poor. Chemical and electrochemical instabilities of cell components are partially responsible for the poor cell performance.<sup>9-11</sup> Electrolytes and polymer binders are readily attacked by the highly nucleophilic anion O<sub>2</sub><sup>-</sup> or singlet oxygen species  ${}^{1}O_{2}$  to generate unfavorable side products, which is harmful to the reversible charge capacity and overall cell performance.<sup>12,13</sup> In addition, Na metal degradation caused by contaminants (e.g.,  $O_2$ ,  $O_2^-$ , and  $H_2O$ ) and Na dendrite growth are two main reasons for the premature cell death that cannot be neglected.<sup>14–19</sup> Nonetheless, it is widely accepted that the properties of the air electrodes where the oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) take place are primarily affecting the electrochemical performance of  $Na-O_2$  cells.

Unlike Li-O2 batteries in which the cathodes have minor effects on the growth of toroidal Li<sub>2</sub>O<sub>2</sub>, which is reported as the only discharge product, the compositions and morphologies of the discharge products in Na-O2 batteries are highly dependent on the nature of the air electrodes. As reported by Wang et al., Na2O2·2H2O and NaOH were identified as major discharge products of Na-O2 batteries with a CoO/CoP electrocatalyst.<sup>20</sup> Ma and co-workers constructed air electrodes with a porous CoB catalyst that produced both NaO<sub>2</sub> and  $Na_2O_2$  during the discharge process of the  $Na-O_2$  batteries.<sup>21</sup> Different to the formation of micrometer-sized NaO<sub>2</sub> on the carbon paper (CP) cathode through a solution-mediated path, Lutz et al. found that the introduction of Au on CP resulted in the formation of NaO<sub>2</sub> flakes through a surface-mediated route, accompanied by a significant decrease in capacity.<sup>22</sup> Compared with Na<sub>2</sub>O<sub>2</sub>, Na<sub>2</sub>O<sub>2</sub>·2H<sub>2</sub>O, NaOH, and Na<sub>2</sub>CO<sub>3</sub>,

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Figure 1. Schematic illustration of the 3D-printed "O<sub>2</sub> breathable" air electrodes for Na-O<sub>2</sub> batteries.

microsized NaO<sub>2</sub> is more desired as a low overpotential and good capacity retention are hardly achieved simultaneously once other products are produced. Therefore, the fabrication of air electrodes with favorable surface chemistries for reversible formation and decomposition of cubic NaO<sub>2</sub> is crucial to achieve high-performance Na $-O_2$  batteries.

In addition to the cathode surface properties, a rationally designed architecture could be important for fully utilizing the air electrode.<sup>23–25</sup> Due to the transport limitation of  $O_2$  within the organic electrolytes, the NaO<sub>2</sub> particles are predominantly deposited in the electrode region with sufficient exposure to O2. The accumulation of NaO2 particles on the oxygen side of cathode can clog the electrode surface that restricts O2 access in the interior air electrode, resulting in the premature termination of the discharge process and underutilization of the air electrodes.<sup>25–27</sup> Even the H23 CP cathode with large pores on the scale of tens of micrometers shows no exception, with a Na–O<sub>2</sub> battery capacity of only  $\sim$ 50% of the theoretical value.<sup>6</sup> Nichols et al. verified that the discharge capacity of Na-O<sub>2</sub> batteries can be improved by increasing the oxygen partial pressure as it changed the concentration gradient for faster oxygen diffusion in the organic electrolyte.<sup>26</sup> By fabricating a self-stacked nitrogen-doped carbon nanotube air electrode, Sun et al. further highlighted the importance of rapid  $O_2$  and  $Na^+$  transportation within the air electrode.<sup>24</sup> However, studies of the fabrication of engineered air electrodes with effective O2 transport channels are relatively scare, and limited O2 mass transportation within the air electrode is still a substantial challenge, especially the thick cathode.<sup>28,29</sup> Additive manufacturing, also known as a 3D printing technique, has attracted an enormous amount of attention in the energy storage field due to its feasibility in fabricating a complex 3D architecture.<sup>30–34</sup> Among various printing materials, graphene oxide (GO) has shown unique viscoelastic properties and printing capabilities when dispersed in H<sub>2</sub>O at a high concentration.<sup>35</sup> Moreover, the electrical conductivity of the

GO can be retrieved after thermal reduction, with the formation of the rGO electrode. Because highly concentrated GO ink can be directly printed into fine filaments, 3D periodic rGO-based air electrodes with the desired architecture and thickness can be well patterned through careful control of the printing parameters.

Herein, we first fabricate a novel "O2 breathable" air electrode by 3D printing for high-performance superoxidebased Na-O<sub>2</sub> batteries. The 3D printed air electrode has a stacked mesh structure with macroscale open pores and interconnected conductive filaments composed of rGO sheets. The vertical open channels across the electrode facilitate continuous O<sub>2</sub> access, promising a full utilization of the active sites on the air electrode. Additionally, the micropores among the rGO sheets provide sufficient space for electrolyte permeation and NaO<sub>2</sub> accommodation. The efficiently packed rGO sheets also ensure sufficient electronic conductivity within the 3D architecture. Consequently, a high specific capacity of 13484.6 mAh  $g^{-1}$  (9.1 mAh cm<sup>-2</sup>) can be achieved at 0.2 A  $g^{-1}$ . Unprecedentedly stable performance is achieved over 120 cycles with a cutoff capacity of 500 mAh  $g^{-1}$  at 0.5 A  $g^{-1}$ . The diameter of the  $O_2$  channels in the air electrode is optimized on the basis of the balance between electronic conductivity and O<sub>2</sub> transportation. This work clearly elucidates the importance of the rational design of the air electrode structure for realizing high-performance  $Na-O_2$  batteries. The emerging 3D printing technique combined with a freeze-drying procedure is demonstrated to be a powerful tool for fabricating effective air electrodes with hierarchical pores.

#### EXPERIMENTAL SECTION

Graphene Oxide (GO) Ink Preparation and Air Electrode Preparation. GO sheets were prepared by the modified Hummers method according to a previous report.<sup>7</sup> Then, the GO dispersion was washed with distilled water until the pH reached 7.0 and then collected by centrifugation to achieve an ~15.0 mg mL<sup>-1</sup> GO ink. No



Figure 2. Top-view SEM images of (a and d) 3DP-NP, (b and e) 3DP-SP, and (c and f) 3DP-LP air electrodes at different magnifications (insets in panels a-c are optical images of the 3D-printed electrodes). Cross-sectional SEM images of (g) 3DP-NP, (h) 3DP-SP, and (i) 3DP-LP cathodes.

binder was used for the printing ink preparation. Next, the ink was loaded into a 3 mL syringe and extruded through a 300  $\mu$ m diameter nozzle. The 3D printed air electrodes with no open pores (3DP-NP), small open pores (3DP-SP), and large open pores (3DP-LP) were printed with an overall diameter of 10 mm at a print motion speed of 8 mm s<sup>-1</sup>, and the diameter of the pores was controlled by changing the distances between the adjacent filaments. The printed GO-based patterns were freeze-dried for 24 h and subsequently thermally reduced at 800 °C in a H<sub>2</sub>/Ar atmosphere for 2 h to obtain the rGO-based air electrodes.

**Materials.** The 3D-printed electrodes were used as the cathode in the Na $-O_2$  batteries. CP purchased from Fuel Cell Store was used as the anode protective layer without further treatment. Diethylene glycol dimethyl ether (DEGDME, reagent grade  $\geq$ 98%, Aldrich) was dried by freshly activated molecular sieves (4 Å, Aldrich) for 2 weeks before use. Sodium triflate (NaSO<sub>3</sub>CF<sub>3</sub>, Aldrich) was dried under vacuum at 80 °C for 1 week.

Battery Assembly and Electrochemical Measurements. The electrochemical performance of Na-O2 batteries was evaluated with Swagelok-type cells. The assembly of cells has been described in detail in our previous work.<sup>18</sup> Briefly, the Na-O<sub>2</sub> cell in this work was composed of a CP interlayer-protected Na anode, a glass fiber separator, and a 3D-printed air electrode. The configuration of the Na-O<sub>2</sub> batteries is shown in Figure S1. The electrolyte was 1 M NaSO<sub>3</sub>CF<sub>3</sub> dissolved in DEGDME. The same amount of electrolyte (100  $\mu$ L per cell) was added in the control. The electrolyte preparation and battery assembly were carried out in an Ar-filled glovebox with oxygen and water contents of <0.1 ppm. The Na-O<sub>2</sub> cells were operated under static O2 with the pressure of 1.5 atm in a homemade testing box. Each Na-O2 cell was stabilized for 1 h at room temperature before being tested. The galvanostatic dischargecharge tests were carried out using an Arbin BT-2000 battery testing system.

**Material Characterization.** The morphologies and structures of air electrodes, as well as the discharge product, were characterized by a Hitachi S-4800 field emission scanning electron microscope (SEM) and transmission electron microscopy (TEM, JEOL 2100F). X-ray diffraction (XRD) (Bruker D8 Advance) with Cu K $\alpha$  radiation was used for structural characterization, and the data were collected from 30° to 70° in  $2\theta$  at a scanning rate of 1° min<sup>-1</sup>. The Raman spectra were recorded on a HORIBA Scientific LabRAM Raman

spectrometer equipped with a 532.03 nm laser. X-ray photoemission spectroscopy (XPS) was carried out with a Kratos Axis Ultra Al- $\alpha$  spectrometer operated at 14 kV. The surface area and pore volume of three air electrodes were studied by N<sub>2</sub> adsorption/desorption using the Brunauer–Emmett–Teller (BET, Micromeritics ASAP2020) method. In this study, the disassembly of the Na–O<sub>2</sub> batteries was carried out in an Ar-filled glovebox. The discharged/charged electrodes were washed with fresh DEGDME to remove any residual NaSO<sub>3</sub>CF<sub>3</sub> salt and then thoroughly dried in a vacuum chamber before SEM, XRD, and Raman measurements. Leak-tight XRD and Raman sample holders were used to prevent the exposure of air during sample testing.

## RESULTS AND DISCUSSION

The fabrication of the free-standing " $O_2$  breathable" Na- $O_2$ battery cathode is schematically illustrated in Figure 1. A homogeneous GO ink was prepared with the desired rheological properties. Then, the stacked mesh structure of GO was printed layer by layer through a nozzle ( $\emptyset = 300 \ \mu m$ ). After the ink solvent of H<sub>2</sub>O had been removed by freezedrying for 24 h, the dried GO structure underwent a thermal annealing process at 800 °C in a Ar/H<sub>2</sub> atmosphere to yield the 3D rGO Na-O<sub>2</sub> cathodes. For comparison, the 3DP-NP, 3DP-SP, and 3DP-LP air electrodeswere prepared via an identical procedure except for the different spacing between adjacent filaments. It should be noted that the introduction of macro open pores into the air electrode is difficult to realize by the traditional electrode fabrication methods.<sup>36</sup> Additionally, different to the dip-casting method, no polymer binder was involved during the preparation of 3D-printed air electrodes because the highly concentrated GO ink provides the prerequisite viscosity to bind the GO nanosheets together. The binder-free feature of the 3D-printed air electrodes not only is favorable for increasing the electrode energy density but also can eliminate the binder-related parasitic reactions induced by the nucleophilic attack of  $\hat{O}_2^-$  on binders in Na-O<sub>2</sub> batteries.<sup>37-40</sup>



**Figure 3.** Initial discharge–charge profiles of (a) 3DP-NP, (b) 3DP-SP, and (c) 3DP-LP cathodes at current densities of 0.2, 0.5, 1, and 2 A g<sup>-1</sup>. (d) Initial discharge–charge profiles of 3DP-NP, 3DP-SP, and 3DP-LP cathodes that were extracted from panels a–c at a current density of 0.5 A g<sup>-1</sup>. (e) Areal specific capacity of Na–O<sub>2</sub> cells with three different cathodes. (f) Comparison of the rate performance of the 3DP-SP cathode from this work with those of other reported rGO-based cathodes.

Raman characterization was conducted to investigate the structural changes of GO during the reduction process. As shown in Figure S2, GO showed broad D (1350 cm<sup>-1</sup>) and G  $(1587 \text{ cm}^{-1})$  bands before the thermal treatment, which is a typical Raman spectrum of GO.41-43 After the thermal reduction, the peaks became sharper and the full width at half-maximum for both D and G bands decreased, suggesting a higher degree of graphitization of the rGO air electrode. Additionally, the increase in the intensity ratio  $(I_D/I_C)$  from 0.93 of GO to 1.05 of rGO can be attributed to the presence of unrepaired defects that remained on rGO after the removal of oxygen-containing functional groups. The removal of oxygencontaining functional groups after reduction can be further confirmed by the remarkable increase in the atomic C/O ratio in the normalized wide-scan survey XPS spectra of rGO (Figure S3). On the basis of the deconvoluted XPS spectra of the C 1s and O 1s regions, the oxygen-containing functional groups, including C=O, COH, and COOH groups, can be partially removed during the thermal reduction process. It is noteworthy that thermal annealing not only can improve the electrode electrical conductivity (Figure S4) but also is favorable for minimizing the undesired reactions catalyzed by oxygen-containing functional groups at the air electrodes during the ORR process of Na-O<sub>2</sub> batteries.<sup>44</sup>

The microstructure of the as-prepared rGO air electrodes was characterized by SEM as shown in Figure 2. Top-view SEM images of 3DP-SP and 3DP-LP cathodes show the stacked mesh structure with macroscale open channels for  $O_2$ passage and conductive filaments (~300  $\mu$ m) of rGO sheets. The diameters of the open channels for 3DP-SP and 3DP-LP electrodes are approximately 350 and 520  $\mu$ m, respectively; no obvious gap was observed between adjacent filaments for the 3DP-NP electrode (Figure 2a–c). Despite the different macroscopic channels introduced by 3D printing, similar honeycomb porous microstructures were constructed in three air electrodes (Figure 2d-f). The presence of microscale pores in the air electrodes can be attributed to the removal of the ice template during the freeze-drying procedure. The icetemplating mechanism can force the GO sheets to align along the growing boundaries of the ice crystals, and thus, the restacking of the GO sheets under the effect of van der Waals or capillary force can be prevented.<sup>35,41,45</sup> The nitrogen adsorption/desorption isotherms of 3DP-NP, 3DP-SP, and 3DP-LP in Figure S5 indicate the presence of both macropores (pore diameter of >50 nm) and mesopores (pore diameters between 2 and <50 nm), and three electrodes possess similar BET surface areas of 342.8, 362.6, and 369.6 m<sup>2</sup> g<sup>-1</sup>. The resultant mesopores contributed to the high degree of exposure of active sites on cathodes for ORR and OER and, at the same time, micrometer-sized pores that are favorable for accommodating insoluble NaO<sub>2</sub>. Additionally, it is worth noting that the hierarchical structures of air electrodes were robust after freeze-drying and thermal reduction (Figure S6 and insets of panels a-c of Figure 2), even though no polymer binder was used, which is urgently desired for Na-O<sub>2</sub> batteries.

The cross-sectional SEM images of three different air electrodes (Figure 2g–i) displayed a similar thickness of ~600  $\mu$ m, which are thicker than the electrodes fabricated by the conventional casting method.<sup>36</sup> The comparable electrode thickness can minimize the effect of electronic transmission efficiency on the performance of Na–O<sub>2</sub> batteries among the three air electrodes. Excellent affinity without obvious boundaries was observed between the adjacent printing layers in the three air electrodes. The structural unity and highly interconnected 2D rGO sheets with diameters of ~5  $\mu$ m ensured efficient electronic conduction throughout the electrode (Figures S7 and S8), and at the same time, infusion of a liquid organic electrolyte into this structure yielded



**Figure 4.** SEM images of (a-c) the fully discharged 3DP-NP cathode and (d-f) the partially discharged 3DP-SP cathode at 0.2 A g<sup>-1</sup> with focuses on the O<sub>2</sub> accessible surface (a and d), cross section close to the side of O<sub>2</sub> flow (b and e), and cross section near the separator side (c and f). (g) SEM image and corresponding EDX elemental mappings of the discharged 3DP-SP cathode. The discharge capacities of both 3DP-NP and 3DP-SP cathodes are 4613 mAh g<sup>-1</sup>.

smooth Na<sup>+</sup> transport pathways. The macro open channels in 3DP-SP and 3DP-LP electrodes that penetrated across the thickness of the air electrodes are beneficial for sufficient  $O_2$  access during the ORR and OER processes. Meanwhile, the micro spacings are also distributed throughout the depth of the rGO filaments, providing a benefit for the full utilization of an air electrode during the discharge and charge process (Figure S9). Intuitively, the favorable hierarchical porous electrode with an interconnected conductive network and efficient  $O_2$  transportation channels can reduce the internal cell resistance, ensure the high availability of the active sites, and thus improve the overall performance of Na $-O_2$  batteries.

The electrochemical performance of Na-O2 batteries with three different air electrodes was tested in the voltage range of 1.5-4.5 V at different current densities. Note that the electrically connected CP interlayer with Na metal as the protected anode is employed when assembling the  $Na-O_2$ cells, to prevent Na dendrite growth and alleviate anode degradation.<sup>17,18,46</sup> As shown in Figure 3a-c, the Na-O<sub>2</sub> batteries with different air electrodes exhibited similar discharge and charge voltage profiles except for the total specific capacities, which indicated no obvious difference in reaction mechanism during their ORR and OER processes. At different current densities of 0.2, 0.5, 1, and 2 A g<sup>-1</sup>, the 3DP-SP air electrodes delivered initial discharge capacities of 13484.6, 11935.3, 7939.6, and 2841.4 mAh g<sup>-1</sup>, respectively, whereas the 3DP-NP electrodes exhibited significantly decreased discharge capacities of 4385.6, 3425.8, 1890.5, and 865.9 mAh  $g^{-1}$ , respectively. Because the three air electrodes possess similar mesopores and micrometer pores, the absence or presence of large open pores on air electrodes should be responsible for the distinct discharge capacities of Na-O<sub>2</sub> batteries. While it is noticeable that the discharge capacities of the 3DP-LP air electrode were slightly lower than those of the 3DP-SP electrode (Figure 3b,c). The initial discharge-charge profiles of the Na-O<sub>2</sub> batteries based on three air electrodes at  $0.5 \text{ A g}^{-1}$  were extracted from Figure 3a-c with a cutoff capacity of 3000 mAh g<sup>-1</sup>. As shown in Figure 3d, the degrees of voltage polarization of the 3DP-SP and 3DP-LP air electrodes were significantly smaller than that of the 3DP-NP air electrode, consequently yielding higher round-trip energy efficiencies. While the 3DP-LP air electrode exhibited an overpotential slightly larger than that of the 3DP-SP electrode at 0.5 A g<sup>-1</sup>, this difference was more obvious at a higher current density of 1 A g<sup>-1</sup> (Figure S10), indicating that the different sizes of open channels had an influence on the internal resistance of the electrodes.

Compared to the 3DP-NP electrode, the enhancement of discharge capacities as well as the ORR/OER kinetics of the 3DP-SP and 3DP-LP air electrodes can be attributed to their efficient O2 transport across the electrode from the macro open channels. However, the increase in open pore size results in a higher porosity and less conductive pathways in the 3DP-LP air electrode than in the 3DP-SP electrode, which was adverse to the electronic conduction within the electrode<sup>43</sup> and thus led to the relative higher discharge-charge overpotential of the 3DP-LP air electrode. In addition, even though the O<sub>2</sub>breathing electrodes have been highly utilized, the high porosity of 3DP-LP cathodes could eventually limit the areal discharge capacity due to low carbon loading and insufficient active surface area. Overall, the 3DP-SP electrodes, which had maximized the active rGO surface with appropriate O<sub>2</sub>breathing capability, exhibited the highest areal capacities among three designs of air electrodes at all current densities (Figure 3e). Specifically, the 3DP-SP electrode achieved a high areal capacity of 9.1 mAh cm<sup>-2</sup> at 0.2 A g<sup>-1</sup>, whereas the 3DP-NP and 3DP-LP air electrodes delivered only 5.3 and 5.8 mAh cm<sup>-2</sup>, respectively. Compared to the reported rGO-based cathode for non-aqueous Na–O<sub>2</sub> batteries,  ${}^{36,47-51}$  the 3DP-SP air electrode demonstrates substantial superiority in specific capacities at all current rates (Figure 3f), benefiting from the well-designed O2 breathing channels and sufficient active surface. It is also noteworthy that the short-circuiting issue can be completely eliminated due to the employment of a CP

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**Figure 5.** (a) Cycling performance of Na–O<sub>2</sub> batteries using 3DP-NP, 3DP-SP, and 3DP-LP cathodes with a limited discharge capacity of 500 mAh  $g^{-1}$  at 500 mA  $g^{-1}$ . Corresponding discharge–charge profiles of (b) 3DP-NP and (c) 3DP-SP air electrodes at different cycles. (d) Cycling performance of the 3DP-SP electrode at 1000 mA  $g^{-1}$  with a limited discharge capacity of 500 mAh  $g^{-1}$ . (e) XRD patterns and (f) Raman spectra of 3DP-SP electrodes at different discharge–charge states upon cycling at 500 mA  $g^{-1}$  by curtailing the discharge capacity to 500 mAh  $g^{-1}$ .

interlayer, which can facilitate Na deposition within its 3D structure, contributing to the high reversibility of  $Na-O_2$  batteries (Figure S11).

To further understand the different discharge capacities between 3DP-NP and 3DP-SP air electrodes, two typical electrodes were disassembled for morphological investigations after discharging at 0.2 A  $g^{-1}$ . Panels a-c of Figure 4 depict the microstructures of the fully discharged 3DP-NP electrode and discharge products determined by SEM. It can be clearly observed that the outer surface (the side facing  $O_2$  flow) of the air electrode was covered by numerous NaO2 cubes with dimensions of >20  $\mu$ m. Such large cubic discharge products are similar to those observed on carbon paper cathodes in our previous report.<sup>18</sup> The cross-sectional SEM images indicated a spatial variation in the distribution and size of NaO<sub>2</sub> cubes across the 3DP-NP electrode. Medium-sized NaO<sub>2</sub> cubes with an average dimension of ~15  $\mu$ m were dispersed in fitting pores of the electrode close to  $O_2$  flow (Figure 4b), while the amount of NaO<sub>2</sub> cubes substantially decreased toward the separator side, indicating incomplete utilization of the 3DP-NP air electrode. The decreasing degree of deposition of NaO<sub>2</sub> from the O<sub>2</sub> accessible side to the separator side was consistently observed across the 3DP-NP electrode (Figure S12). Few NaO<sub>2</sub> were observed in the regions approaching the separator. In contrast, with the same discharge capacity, the discharge product NaO2 deposited across the depth of the entire 3DP-SP air electrode (Figure S13). SEM images in Figure 4d-f clearly show the uniform and widespread occurrence of cubic NaO2 deposits across the depth of the 3DP-SP air electrode, but with decreasing dimensions. The small cubic deposits ( $\leq 5 \mu m$ ) on the 3DP-SP air electrode toward the separator side were confirmed to be NaO2 by energy dispersive X-ray spectroscopy (EDX) elemental mapping images in Figure 4g. Unlike the pore clogging

behaviors in the 3DP-NP electrode, the dissolved  $Na^+-O_2^-$  can be continuously deposited onto the existing small  $NaO_2$  cubes upon further discharging due to efficient  $O_2$  access. This also explains the high discharge capacity achieved by the 3DP-SP air electrodes.

On the basis of the SEM observations, we can relate the distinct NaO<sub>2</sub> distributions to the different O<sub>2</sub> accessibilities across the two air electrodes. Due to the easy access of O<sub>2</sub> and fast electronic conductivity, the NaO<sub>2</sub> cubes were preferentially formed on the outer surface of both 3DP-NP and 3DP-SP large electrodes (20  $\mu$ m) (Figure 4a,d). However, due to the pore clogging effect, the accumulation of the discharge product impeded O2 transfer within the 3DP-NP air electrode for further discharge. As a result, active sites away from the surface were not fully utilized. In the case of the 3DP-SP air electrode, the vertical open pores in the electrode act as the O<sub>2</sub> transport channels, ensuring continuous O<sub>2</sub> access during the proceeding discharge process. Hence, full utilization of active sits on the electrode as well as a high discharge capacity can be achieved. A similar result also can be observed for the 3DP-LP air electrode due to the positive effect of the open O2 channels (Figure S14).

The cycling performance of Na–O<sub>2</sub> batteries using 3DP-NP, 3DP-SP, and 3DP-LP electrodes is shown in Figure 5a. At 0.5 A g<sup>-1</sup> with a limited capacity of 500 mAh g<sup>-1</sup>, the 3DP-SP cell exhibited the longest cycle life of the three of 122 cycles, which substantially surpassed the 39 cycles of the 3DP-NP cell and the 105 cycles of the 3DP-LP cell. Notably, the discharge–charge profiles of the 3DP-SP cell were highly stable during cycling, and the terminal discharge voltage was still >2.0 V at 80 cycles. In a manner consistent with the rate profiles in Figure 3a–c, the 3DP-NP cell exhibited a discharge–charge overpotential that was larger than that of the 3DP-SP and 3DP-LP cells (Figure 5b,c and Figure S15). As the thicknesses of the

three air electrodes were comparable,  $O_2$  accessibility and electronic conductivity rather than ionic resistance were responsible for the different cycle lives. Even with a limiting discharge capacity of 500 mAh g<sup>-1</sup> at a higher current density of 1000 mA g<sup>-1</sup>, a Na–O<sub>2</sub> battery based on the 3DP-SP cathode also achieved excellent cycling stability over 100 cycles (Figure 5d and Figure S16). These results again highlight the rational design of the air electrode that significantly enhanced the electrochemical performance of Na–O<sub>2</sub> batteries.

Figure 5e shows the XRD patterns of the 3DP-SP air electrode at different discharge-charge cycles to evaluate the reversibility of the electrochemical products. Regardless of the first or 50th discharge state, the characteristic peaks of crystalline NaO<sub>2</sub> can be observed clearly. Both the positions and the intensities of the reflections are in good agreement with the previous reports.<sup>27,52</sup> The disappearance of the NaO<sub>2</sub> characteristic peaks at the first and 50th charge states indicated the high reversibility of NaO<sub>2</sub>, as also evidenced by the absence of cubic particles on the SEM image of the recharged air electrode (Figure S17). We note that small peaks of  $Na_2O_2$ .  $2H_2O$  appear at  $2\theta \approx 37.1^\circ$ ,  $40.6^\circ$ , and  $41.2^\circ$  after 50 cycles, which can be ascribed to the reaction between NaO<sub>2</sub> and water that forms gas or an electrolyte during cycling.<sup>53,54</sup> The highly reversible formation and decomposition of NaO<sub>2</sub> on the 3DP-SP electrode were further confirmed by Raman analyses (Figure 5f). The Raman spectra of the discharged 3DP-SP air electrodes exhibited strong signals of NaO<sub>2</sub> at 1156 cm<sup>-1</sup> that disappeared after charge. The XRD and Raman results complementarily proved that the high discharge and charge capacities of the 3DP-SP air electrode were did indeed result from the desirable formation and decomposition of NaO<sub>2</sub>.

As opposed to the peroxide-based Na-O2 batteries that require a high charge voltage (>3.5 V) like Li-O<sub>2</sub> batteries, the electrochemical reduction of NaO2 exhibits a low charge overpotential. Therefore, the concerns about electrolyte decomposition and singlet <sup>1</sup>O<sub>2</sub> generation during charging at high voltages were avoided.<sup>13</sup> Additionally, the binder-free feature of the 3D-printed air electrodes eliminated possibly undesirable side reactions that could be induced by proton abstraction of  $O_2^-$  from the binder polymer backbone. However, it should be noted that the formation of NaO<sub>2</sub> via the solution-mediated path results in a large amount of the dissolved  $O_2^{-}$  intermediate in the organic electrolyte. Therefore, the degradation of the air electrode induced by the  $O_2^$ radical cannot be avoided, and the active sites on the electrode surface will be gradually covered by the filmlike side products, especially after long-term cycling (Figure S18). Additionally, the dissolved  $O_2^-$  intermediate tends to migrate from the cathode to the Na anode, which not only induces severe Na anode corrosion but also results in reversible charge capacity loss and inferior Coulombic efficiency (<100%) (Figure 5b,c).<sup>15,18</sup> Note that the incomplete decomposition of  $NaO_2$ also contributes to the limitted Coulombic efficiency of Na-O2 batteries. Except for the issues mentioned above, the structural changes of the air electrode during cycling may also responsible for the limited cycle life. Because the discharge product of Na-O<sub>2</sub> batteries is cubic NaO<sub>2</sub>, and the NaO<sub>2</sub> size can be 1-50  $\mu$ m. With the repeated formation and decomposition of NaO<sub>2</sub> during cycling, the pore structure of the air electrode may change or even cause slight pore structure collapse, which is adverse to the stable cycling of  $Na-O_2$  batteries. Additionally, the  $Na-O_2$  battery is an open system, so the effect of organic electrolyte evaporation as well

as electrolyte decomposition/consumption also cannot be neglected. All of these factors inevitably attenuate the cycle life of  $Na-O_2$  batteries.

In fact, the electrochemical performance of the  $Na-O_2$ batteries is also comprehensively affected by the mass transport of  $O_2/Na^+$  and the electronic conductivity within the cathode. The highly microporous structure of 3DP-NP enabled thorough permeation of the electrolyte in the electrode with a large active surface area, which benefited the rapid access of Na<sup>+</sup>. However, electrolyte flooding conversely limited O<sub>2</sub> transport. The accumulation of insoluble discharge products on the open surface of the air electrode had blocked the passage of  $O_2$  to the inner electrode for complete discharge. Hence, the 3DP-NP cathode exhibited poor rate capability and low capacity. With respect to the 3DP-LP cathode, the entire air electrode was accessible to both the organic electrolyte and  $O_2$  due to the microporous framework and additional  $O_2$ pathways. The sufficient O2 and Na<sup>+</sup> access to the active surface led to a discharge capacity that was higher than that of the 3DP-NP air electrode; however, the total active rGO surface and electronic pathways were limited in the 3DP-LP cathode when the O<sub>2</sub> open channels were too large, causing drawbacks in Na-O2 cell performance. The impressive performance of the 3DP-SP cathode was attributed to the fine balance between efficient ionic/electronic conductions and enhancement of O<sub>2</sub> diffusion kinetics within the electrode. The appropriate proportion of O2 pathways in the electrode facilitated continuous ORR in the air electrode, alleviating the concern of rate-limiting O2 transport that had been demonstrated by the 3DP-NP cathode. Moreover, the effective areal mass loading of the 3DP-SP cathode was much higher than that of the 3DP-LP electrode, providing a significant improvement in electronic conduction and active surface area. It should be noted that the optimized electrode in this work was the 3DP-SP electrode, but the optimal size and proportion of open O<sub>2</sub> channels may vary depending on the 3D printing materials, resolution, thickness, and drying methods for the electrodes. Upon development of 3D printing techniques that can be used for thicker electrodes with smaller O2 open channels, further enhancements in areal capacity and rate capability for Na-O<sub>2</sub> batteries are expected.

#### CONCLUSION

In summary, we designed and fabricated a free-standing "O<sub>2</sub> breathable" air electrode with micro open pores by a 3D printing technique for high-performance Na-O2 batteries. Unlike the uniform microporous 3DP-NP air electrode, the built-in O2 pathways in the "O2 breathable" cathode facilitated sufficient  $O_2$  access even in the inner cathode, preventing surface clogging by discharge products and the premature ceasing of discharge. Moreover, an appropriate proportion between rGO active frameworks and O<sub>2</sub> open channels in the 3DP-SP electrode (compared to the 3DP-LP electrode with large O2 channels and less active rGO loading) endowed the cathode with an effective balance between electronic conductivity and O2 access. In terms of synergistic results, the 3DP-SP air electrode achieved high utilization and a remarkable capacity of 13484.6 mAh  $g^{-1}$  (9.1 mAh cm<sup>-2</sup>) at 0.2 A g<sup>-1</sup>. Stable cycling performance was demonstrated over 120 cycles with a cutoff capacity of 500 mAh  $g^{-1}$  at 0.5 A  $g^{-1}$ , which is among the values of top-class superoxide  $Na-O_2$ batteries. The ingenious application of 3D printing to demonstrate the importance of air electrode design with sufficient  $O_2/Na^+$  transportation and excellent electronic conductivity shall inspire the development of high-performance Na-O<sub>2</sub> batteries.

## ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.chemmater.9b05360.

Additional experimental methods; optical, SEM, and TEM images; and additional electrochemical performance characterization (PDF)

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## **Author Contributions**

X.L. and X.S. conceived and designed the experimental work with the help of J.W. and X.G., who printed the air electrodes. X.L. and Q.S. participated in analyzing the experimental results. S.W. and X.Y. helped with the schematic diagram. C.W. performed the XRD characterization, and Y.Z. helped with the Na anode protection. X.L., Q.S., C.Z., J.L., and R.L. participated in the discussion of the data. X.S. supervised the overall project. All authors have given approval to the final version of the manuscript.

#### Notes

The authors declare no competing financial interest.

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