Interrogation of the Reaction Mechanism in a Na–O₂ Battery Using *In Situ* Transmission Electron Microscopy

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morphology of discharge products are largely unknown for Na– O_2 batteries. Here we report a reversible oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) process in a sodium-oxygen battery observed using *in situ* environmental-transmission electron microscopy (TEM) experiment. The reaction mechanism and phase evolution are probed using *in situ* electron diffraction and TEM imaging. The reversible ORR and OER cycling lies upon the nanosized copper clusters that were formed *in situ* by sodiation of CuS. *In situ* electron diffraction revealed the formation of NaO₂ initially, which then disproportionated into orthorhombic and hexagonal Na₂O₂ and O₂. Na₂O₂ was the major final ORR product that uniformly



covered the whole wire-shape cathode. This uniform product morphology largely increased the application feasibility of Na– O_2 batteries in industry. In the following OER process, the Na₂O₂ transformed to NaO₂, which resulted in volume expansion at first, and then the NaO₂ decomposed to sodium ions and O₂ gas. Galvanostatic charge/discharge profiles of CuS in real Na– O_2 cells revealed a maximum capacity over 3 mAh cm⁻² with a discharge cutoff voltage of 1.8 V and high cycling stability. The nanosized copper catalyst plays a dominating role in controlling the morphology, chemical composition of discharge products, and reversibility of this Na– O_2 battery. Our finding shines light on the exploration of effective catalysts for the Na– O_2 battery. KEYWORDS: in situ TEM, Na– O_2 battery, oxygen evolution reaction, oxygen reduction reaction, phase evolution

ecause of their high theoretical energy density, metal-air batteries can greatly extend the driving mileage of electric vehicles per charge and accelerate the development of advanced electrical energy storage system.^{1,2} However, the sluggish oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) kinetics is the bottleneck for successful operation of rechargeable metal-air batteries.³⁻⁷ Catalysts that promote the efficiency and reversibility of both ORR and OER are critically important for a rechargeable metal-air battery. Although precious metal-related catalysts, such as Pt, Pd, Ag-MnOx, or IrO₂, are active OER/ORR catalysts, their large-scale application is hindered by their high cost and scarcity.^{8,9} The catalysts can enhance the power density and modify reaction pathways and product structures.⁹⁻¹¹ Reports show that copper-based catalyst derived from Cu-MOF precursor exhibited boosted ORR activity comparable to commercial Pt/C.¹⁰ There are a number of papers reporting the super effectiveness and possible

mechanism of using copper catalysts for oxygen reduction or evolution reactions. $^{12-17}$

The decomposition of discharge product, such as Li_2O_2 in a $Li-O_2$ battery and Na_2O_2 in a $Na-O_2$ battery, is the most challenging issue in the path to achieve rechargeable performance. Carbon-based catalysts often lead to the formation of Li_2CO_3 and lack stability in the long term. Finding the right catalyst that can efficiently decompose Li_2O_2 or Na_2O_2 is the most important step in the deployment of $Li-O_2$ or $Na-O_2$ batteries. Luo et. al reported the reaction mechanism of $Li-O_2$ batteries, where the RuO_2 acts as the

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Figure 1. (a) TEM image of biomimetic CuS grown along [001] direction; (b) electron diffraction pattern of CuS; (c) HRTEM shows the crystal lattice of CuS and the FFT on the lower corner; (d) HRTEM image of CuS showing (002) crystal planes; (e) EDS elemental mapping showing the Cu, S maps and composite Cu and S map.



Figure 2. (a) Overall TEM image showing the reaction front and the morphology change after sodiation in vacuum; (b) CuS single crystal diffraction pattern; (c) diffraction pattern of the sodiated region; (d) HRTEM showing the formation of Cu crystals formed after sodiation; (e) EELS spectra showing the Cu signal and Na of the sodiated region.

catalyst and LiO_2 and Li_2O_2 formed as major ORR products.¹⁸ The big Li_2O_2/Li_2O bubble-products that appear on the interface between the carbon nanotube and lithium source may cause limited capacity due to limited interface area and storage capacity.¹⁸ Recently, Zhu et. al revealed that cobalt oxide and amorphous lithia-composite can catalyze the reactions between $Li_2O/Li_2O_2/LiO_2$ without formation of oxygen gas during

charge and discharge cycles of a Li– O_2 battery, achieving stable cycling with high capacity. $^{19-21}$

The Na-air batteries often produce a mixture of Na_2O_2 and NaO_2 .^{2,22} According to earlier reports, larger Na^+ ions can stabilize superoxide and peroxide.^{20,21,23–25} Na-air batteries are very attractive due to the lower charging overpotentials than $Li-O_2$ battery due to the major superoxide products. The

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Figure 3. (a-c) TEM images showing the sodiation process of CuS crystal in vacuum; (d-f) after introducing O₂ into the chamber, ORR process took place in O₂, showing the NaO_x formation on top of the sodiated surface; (g) magnified image showing the high-density mesoporous NaO_x particles; (h) magnified image showing the copper clusters showing dark diffraction contrast pointed by the white arrows underneath the mesoporous NaO_x particles; (j) plot of the diameter and sodiation length changes during the sodiation and ORR process; panels a-f share the same scale bar.

successful operation of a Na–O₂ battery depends critically on catalyst's performance, reaction mechanism, product morphology, and electrolyte choice.¹⁹ The reaction pathway and dynamic evolution of the products can be directly observed using *in situ* aberration-corrected environmental transmission electron microscopy (TEM) in an oxygen-gas environment.^{26–29} Here we report an *in situ* TEM study on the Na–O₂ battery with copper-based catalyst. As observed, the Na⁺ diffusion, size, and morphology of copper catalyst govern the complex reaction kinetics and product formation. We successfully identified the mesoporous ORR products, and elucidated the phase transformation and decomposition route of Na₂O₂ species in OER.

RESULTS AND DISCUSSION

The detailed synthesis procedure and morphology characterization of CuS nanowires were reported in our previous publication.³⁰ Figure 1 shows the fresh CuS wires growing along the [001] crystal direction. CuS exhibits single crystalline characteristic with hexagonal lattices as proven by the electron diffraction pattern in Figure 1b and HRTEM and FFT analysis in Figure 1c and d. The single crystalline diffraction pattern indicates that the CuS leaves on the central CuS stem is epitaxial growth. The (002) crystal plane is indexed by HRTEM in Figure 1d. Electron energy dispersive spectroscopy (EDS) analysis revealed the uniform chemical composition of Cu and S along the whole wire.

Figure 2 illustrates the morphology and structural changes of CuS upon Na⁺ insertion. The *in situ* TEM setup used a thin layer of Na₂O as solid state electrolyte. Once the CuS touched

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the Na₂O, the Na⁺ can diffuse through Na₂O into the CuS wires and begin the insertion and conversion reaction with a -2 V applied voltage. As shown in Figure S1, Figure 2a, and Movie S1, the fresh crystalline CuS shows dark diffraction contrast in the bright field TEM image, while the reacted-CuS color became much lighter and curving due to the sodiationinduced elongation. Please note that Figure 2a shows a TEM image of a single CuS wire containing three sets of CuS microplates. Figure 2b shows a single-crystalline-like SAED pattern, indicating some possible distortion and tilted regions. These possible defects caused the extension of diffraction spots in Figure 2b. The single-crystalline-like diffraction spots in the fresh CuS as shown in Figure 2b evolved to a diffused polycrystalline ring pattern corresponding to copper metal and Na₂S after sodiation as shown in Figure 2c. The highmagnification TEM image in Figure 2d clearly exhibits the dark nanocopper metal extruded from the matrix upon sodiation, which mimics the lithiation process reported earlier.³⁰ The electron energy loss spectroscopy (EELS) profile acquired at the sodiated region in Figure 2e clearly identifies the copper metal peak and the underlying Na₂S matrix by Cu L edge and Na K edge.

Please note that such in situ TEM requires a careful calibration of the electron dosage. A threshold of 600 $e^{-}/Å^{2}$ s is found safe, above which the CuS-based air cathode decomposes during ORR as shown in Figure S2. As clearly shown in Movies S1-S3 and Figure 3, the sodiation process produced a composite of copper clusters in a Na₂S matrix, which induced large volume expansion. Interestingly, the large volume expansion is mostly released along the growth direction [001], while it is less pronounced along the diameter direction such as [010] or [100] direction. By tracking the length and diameter of the CuS wire before and after sodiation in Figure S1, the diameter changed from 377 to 401 nm after sodiation, while the length changed from 1003 to 1481 nm. On the basis of the equation volume = length $\times (\pi r^2)$ for such cylinder-like CuS, the volume expansion increased by ~67% of its original volume. Clearly, the elongation along [001] direction dominates the volume expansion. Figure 3 exhibits the ORR process of the Na $-O_2$ battery observed using in situ TEM. First, we sodiated CuS nanowires in vacuum to induce the formation of Cu metallic clusters that acted as catalysts in following ORR and OER. Figure 3a-c reveal the morphology changes of CuS during sodiation in vacuum, which induce elongation and diameter expansion. The black arrow points to the sodiation reaction front. The nanoscale copper clusters on the surface of sodiated CuS are efficient catalysts for ORR and OER. After introducing O2 gas into the TEM during sodiation process, ORR took place to further enhance the energy capacity based on Na-O2 battery mechanism. The diffused Na^+ ions reacted with O_2 to form NaO_x species as ORR products. In sharp contrast with the previous report on using in situ TEM for $Li-O_2$ batteries,¹⁸ the formation of NaO_x particles inside in situ TEM chamber in this study is quite uniform along the CuS wires instead of just on the triphase interface of CuS cathode, O2 gas, and Na/Na2O anode. This is most likely owing to the fast Na⁺ transportation along the nanowire and uniform copper formation over the whole wire after sodiation as shown in Figure 2d. High-resolution TEM image in Figure 3h identifies the copper nanoclusters that shows dark diffraction contrast underneath the as-formed NaO_x particles in ORR. Figure 3J plots the diameter and length of the sodiated region as a function of time. The white

dashed arrow in Figure 3a marked the region, where the diameter measurements were taken. The overall sodiated length quickly reached 3605 nm at 2117s and slowed down afterward. The diameter of the wire swelled to 483 nm at 2117 s after sodiation in vacuum. After releasing O_2 into the chamber, ORR resulted in formation of additional NaO_x particle products and further significant swelling of the diameter to 543 nm at 2480 s. The overall volume expansion is around 200% compared to the fresh CuS, which is less than the reported CuO air cathode.²⁶ The large volume expansions in CuO-based air cathode were caused by the rapid release of gases in the reactions, which pulverized the air cathode itself. Here, CuS-based air cathode is very stable, which does not show large amount of volume expansion and pulverization.

Figure 4 exhibits the ORR and OER process of another CuS wire observed using *in situ* TEM. Through the comparison of



Figure 4. (a) TEM image of another fresh CuS; (b) sodiation of CuS in vacuum; (c) after introducing O_2 into the chamber, ORR took place and TEM image found additional particle-shaped products on the surface of sodiated phase; (d) magnified TEM image of the mesoporous NaO_x particles; (e) *in situ* TEM micrographs of the OER process. Panels a-c share the same scale bar.

the fresh CuS, sodiated phase, and final phase after ORR, additional ball-shaped products grew out of the sodiated CuS surface after ORR. Clearly shown by the high-magnification TEM in Figure 4d, these ball-shaped products are mesoporous. The OER process in O_2 can be visualized in Movie S4 and Figure 4e. Surprisingly, the ball-shaped ORR products first became bigger at 253 s and then slowly decomposed at 979 s finally. One such example is pointed by the black arrow in Figure 4e. On the basis of statistical measurements, we calculated the mean diameter of the mesoporous ball-shaped products, which is around 68 ± 15 nm at 0 s and 78 ± 17 nm at 253 s in OER in Figure 4e. It is evident that the tiny copper catalysts are active and efficient OER electrocatalysts that enhance the reaction kinetics and promote the decomposition of mesoporous Na₂O₂.



Figure 5. Transmission electron diffraction pattern evolutions of (a, b) sodiation process in vacuum; (c-f) ORR process in O_2 ; (h, i) OER process in O_2 ; (g) TEM image of the spherical mesoporous ORR products.



Figure 6. Schematics showing the ORR and OER phase evolution of CuS wires.

In situ diffraction patterns in Figure 5 and Movies S5 and S6 clearly identify crystal structures of the reaction products during ORR and OER process. Figure 5a and b identify the Na₂S and extruded Cu formation after the sodiation of CuS crystal, which is also similar to lithiation of CuS.³⁰ After releasing O_2 into the chamber, the Na₂S began to transform to NaS and NaO_x instantly. A set of diffraction rings in the electron diffraction pattern unambiguously identify the NaO₂, orthorhombic and hexagonal Na₂O₂ phase as ORR products as shown in Figure 5. At first, the dominating product was confirmed to be NaO₂ as shown by a set of diffraction rings in Figure 5c. As ORR proceeded further to 152 s in Figure 5d, most Na₂S transformed to NaS, while Na₂O₂ became the predominant sodium oxide phases. As observed, NaS is a very stable substrate for the nanoscale copper catalysts under ORR

and the subsequent OER process. Following the ORR, the diffraction rings in Figure 5e and f identify the increasing amount of orthorhombic and hexagonal Na_2O_2 phase. In the end, the final product is a composite of hexagonal Na_2O_2 and orthorhombic Na_2O_2 based on the electron diffraction analysis in Figure 5f. First principle calculations showed that NaO_2 is more stable at the nanoscale and requires much smaller nucleation energy than Na_2O_2 .²² Our results are consistent with this theory, as we observed NaO_2 formed initially and then Na_2O_2 dominated in the final products as they grew in size in ORR. In conclusion, *in situ* electron microscopy revealed that the instability of NaO_2 phase led to a phase decomposition into Na_2O_2 and O_2 , which is in agreement with the previously reported results.²⁶ The O_2 gas released in the decomposition of NaO_2 resulted in mesoporous Na_2O_2

product in the end of ORR as shown by the TEM image in Figure 5g and Figure 4d. Figure 5g shows black dots, which are likely due to the tiny amount of Na₂O formed during the reactions. Because of the higher sodium content, it showed up as tiny black dots. Figure S3 exhibits the crystal structural models of reaction products in these processes, including Na₂S, NaS, NaO₂, orthorhombic and hexagonal Na₂O₂ phases.^{31–34}

As observed, the OER can also be reversibly catalyzed by the nanoscale copper catalysts as shown in Figure 5h and i and Movie S4. Theoretically, the decomposition of Na₂O₂ phase can go through two different routes in OER. The first route is the direct decomposition into sodium ions and oxygen gas $(Na_2O_2 \leftarrow \rightarrow O_2 + 2Na^+ + 2e^-)$. The second route contains two steps: the first step is the transformation to NaO₂ intermediate phase (Na₂O₂ + O₂ \rightarrow 2NaO₂); then the second step requires transfer of one additional electron to the NaO₂ intermediate to form Na⁺ and O₂ gas (NaO₂ \rightarrow Na⁺ + $O_2 + e^-$). The electrochemical reaction (NaO₂ $\leftarrow \rightarrow$ Na⁺ + O₂ $+ e^{-}$) has been proven as a reversible redox reaction with little overpotential $(\sim 200 \text{ mV})$.^{20,35} The electron diffraction patterns in Figure 5h and i clearly identify the formation NaO₂ intermediate phase with a number of diffraction rings corresponding to (212), (002), (121), (120), (101), and (020) crystal planes of NaO₂. In the end of OER in Figure 5i, the Na₂O₂ phases show only one very weak diffraction rings, while the predominant product is the NaO₂ phase, which can then be decomposed to sodium ions and oxygen gas as proven by Figure 4. The phase transformation schematic is presented in Figure 6. The electron diffraction analysis in Figure 5 corresponds well to the in situ TEM imaging analysis of OER in Figure 4e, where the Na₂O₂ phases first transformed to NaO₂ with increased volume swelling, and then NaO₂ decomposed and disappear as shown by the phase transformation schematic in Figure 6. When one Na₂O₂ unit cell incorporated more O₂ and became two NaO₂ unit cells, its volume swelled to a bigger size. The volume swelling observed in Figure 4e is intuitively understandable. In addition, in situ TEM imaging in Figure 4 also ambiguously identifies the mesoporous feature of the final Na2O2 products in ORR. The mesoporous products facilitated O₂ gas release and incorporation in ORR and OER; therefore, the high porosity ensures a better reversibility and fast reaction kinetic during the following OER.

In comparison, previous literature showed the formation of big Li_2O_2 bubbles species at the close interface between Li metal and air cathode as final products in the $\text{Li}-\text{O}_2$ battery.¹⁸ The big-bubble-type morphology is not wanted as a final ORR product due to the limited space inside the airbattery itself. The uniformly Cu-decorated NaS wires after sodiation provided an ideal surface sites for these reactions to take place as shown by the schematic in Figure 6. It resulted in more uniform distribution of ORR products as shown in Figure 4, which is most wanted due to the reversibility requirement, space utilization, and full-utilization of catalyst surfaces.^{1,27} The small size and uniform distribution of the asformed mesoporous Na₂O₂ products ensured good reversibility of Na-O₂ battery.

The *in situ* TEM results in Figure 4e confirm that the Na_2O_2 product can decompose well in the OER process with nanoscale copper catalysts. To double confirm the identity of nanoscale copper clusters during ORR and OER, Cu-L edge fine structure comparisons with copper metal, CuS, CuO are carried out in Figure S4. The Cu metal L edge is quite

distinctly different compared with CuS and CuO. The Cu contents after ORR and OER in our cathode are quite similar to Cu metal L edge. Therefore, it also proves the presence of Cu metal nanoclusters during reactions.

In comparison, Liu et. al also reported Na₂O₂ formation when using CuO as air electrode in a Na-O₂ battery.²⁶ However, the ORR resulted in structural breakdown of the CuO wires structure.²⁶ In our experiment, the as-formed nanoscale copper catalysts on NaS wires are stable under ORR and OER conditions, which is a desired property in a long-life battery. In addition, we also compare our CuS-based air cathode with Co₃O₄ air cathode using in situ TEM. As shown in Figure S5, ORR products only form at the interface between the air cathode and Na source with Co₃O₄ air cathode. This is significantly different with the CuS-based air cathode, where uniform formation of ORR products on all surfaces of CuS is observed in Figures 3 and 4. It indicates that CuS-based air cathode has a much higher sodium ion transfer rate than Co₃O₄. A more uniform distribution of ORR products promotes a longer lifetime and bigger energy capacity potential of such air batteries. Especially with CuS-based air cathode, the mesoporous products of Na2O2 species as identified by in situ electron diffraction contributed directly to the reversibility of Na-O2 batteries. As mesoporous structures ensure fast diffusion kinetics of ions, O2, and provide large surface areas for ORR/OER to take place, the controlled product morphology of OER products through the utilization of a nanoscale copper catalyst is inherently related to the catalyzing kinetics, high active surface area, and adsorption of different species during the reaction.

The reversible cycling ability of the Na–O₂ battery using CuS air cathode was proved using *in situ* TEM and galvanostatic discharge and recharge profiles by assembling Na–O₂ batteries using the CuS-based air cathode in Figure 7.



Figure 7. (a-f) Reversible cycling of $Na-O_2$ battery shown by *in situ* TEM.

As shown by the TEM images in Figure 7a, c, and e, after first, second, and third ORR discharges, the ball-shaped NaO_x nanoparticles appeared uniformly on the surface of the air cathode. In contrast, after OER in the first, second, and third cycles in Figure 7b, d, and f, these ball-shaped NaO_x nanoparticles completely disappeared. Please note that the ORR products are very sensitive to electron beam; therefore, the observed formation of ball-shaped ORR products became less with continued cycling. In addition, galvanostatic charge/ discharge profiles of CuS in real $Na-O_2$ cells are shown in

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Figure 8. Galvanostatic charge/discharge profiles of CuS in Na–O₂ batteries. (a) Discharge profile with a cutoff voltage of 1.8 V and a discharge capacity of \sim 3 mAh cm⁻²; (b) discharge/charge profiles with a limited areal capacity of 0.3 mAh cm⁻² at a current density of 0.01 mA/cm⁻²; (c) voltage profiles in different cycles at 0.01 mA cm⁻² with a limited areal charge/discharge capacity of 0.1 mAh cm⁻²; (d) profile of areal current densities and voltages versus time at 0.01 mA cm⁻² with limited charge/discharge time of 10 h.

Figure 8. Figure 8a shows a maximum capacity over 3 mAh cm⁻² at 0.01 mAh cm⁻² with a discharge cutoff voltage of 1.8 V, and the overall discharge time is larger than 300 h. Even for such a long discharge time and a high discharge capacity, the discharge plateau keeps stable at around 2 V. Figure 8b illustrates an intact charge/discharge cycle at 0.01 mA cm⁻² with a limited charge/discharge time of 30 h. Figure 8c and d exhibit the long-term cycling performance of CuS, and the overall working time of the cathode is larger than 600 h. After 30 cycles, the discharge terminal voltage is still higher than 2 V, and the charge terminal voltage stays stable at \sim 4.0 V. The plateau voltage of the first discharge curve is slightly higher than the rest cycles, which may result from the sodiation process of CuS previously mentioned. Furthermore, the theoretical voltage of the discharge reaction to produce Na₂O₂ is 2.33 V. The discharge plateau of CuS air cathode is around 2 V, in agreement with the theoretical voltage of Na₂O₂. The small deviation is caused by the polarization of Na– O_2 systems. In addition, the main charge plateau is at ~4 V, in good agreement with the decomposition voltage of Na_2O_2 ³⁶ and the slight slope in the charge process between 2.5 and 3.65 V may correspond to the decomposition of NaO_{x} . Na₂O₂ is the dominant discharge product, which is in good agreement with the previous literature and our in situ TEM results.^{36–39} Therefore, real-cell measurements are consistent with in situ TEM results showing a major product of Na₂O₂ as ORR discharge products and a reversible cycling of Na-O2 battery using CuS-based air cathode.

CONCLUSIONS

In conclusion, we used *in situ* environmental TEM to directly observe the ORR and OER of a $Na-O_2$ battery using CuS as the air cathode. The extruded copper crystals on the surface acted as efficient catalysts for following ORR and OER. The uniform distribution of copper nanocatalysts and inherent reaction kinetics resulted in uniform formation of mesoporous particle-shaped Na_2O_2 products during ORR. The ORR

products included NaO₂ transient phase, orthorhombic and hexagonal Na₂O₂ phases as identified by electron diffraction analysis. In the following OER process, mesoporous Na₂O₂ transformed to NaO₂ phase first and reversibly decomposed into sodium ions and oxygen gas during OER process. The size, distribution, and composition of electrocatalysts played important role in controlling the morphology and size of the final reaction products. Real-cell test showed reversible ORR and OER cycling and profiles consistent with *in situ* TEM results. Our results provided insights on finding the right catalysts to selectively control the product structure and reversibility of ORR and OER of a rechargeable Na–O₂ battery.

EXPERIMENTAL SECTION

The detailed synthesis procedure and morphology characterization of CuS nanowires was reported in our previous publication.³⁰ In situ TEM was conducted using an FEI G2 Environmental-TEM operating at 200 kV with a PicoFemto scanning tunneling microscopy (STM) holder as shown in Figure S6. All in situ TEM experiments were done through a three-step procedure. (1) First, we sodiated the CuS under a negative bias of -1 to -2 V in vacuum to induce the formation Cu nanocrsytal on the nanowire surface. (2) Then 1 mbar of O2 was introduced to the TEM chamber to initiate the ORR process. In ORR, a constant negative bias of -2 V was applied at the nanowire air cathode side. (3) In the following OER process, a constant positive bias of +4 V was applied at the air cathode to induce the reversible decomposition of ORR products such as Na₂O₂ and NaO₂. Environmental-TEM that is equipped with differential pumps allows the input of O2 gas into the TEM chamber. The oxygen pressure is 1 mbar inside the TEM chamber. A maximum dosage of 200 e/A^2 s was used in the in situ TEM experimental observation to minimize the effect of electron beam dosage. The electrochemical performance of was measured in Na-O2 systems. CuS mixed with super P, polyvinylidene fluoride (weight ratio: 8:1:1), was

coated on carbon paper, which worked as the cathode. Carbon paper served as the current collector and the gas diffusion layer of the cathode. Na metal and glass fiber membrane were employed as the anode and the separator, respectively. Excessive Na was used to exclude the influence of Na anode. 1 M NaTFSI/TEGDME solution worked as the electrolyte. Na $-O_2$ batteries were assembled with 2032 coin-type cells (with holes) in the glovebox. The batteries were tested in the O_2 atmosphere (99.9%), and the pressure of O_2 was 1 bar. The galvanostatic charge/discharge test utilized Neware CT-4008 equipment. The test temperature was around 25 °C.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsnano.0c00283.

In situ TEM observation of sodiation of CuS in vacuum (AVI)

In situ electron diffraction evolution of sodiation of CuS in vacuum (AVI)

In situ TEM observation of sodiation and subsequent ORR in O_2 (AVI)

In situ TEM observation of OER in O_2 (AVI)

In situ electron diffraction evolution of ORR process (AVI)

In situ electron diffraction evolution of OER process (AVI)

In situ TEM observation of ORR process viewed with high electron dosage (AVI)

Additional relevant information regarding ORR and OER process using CuS-based air cathode (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Li, Y.; Lu, J. J. A. E. L. Metal–Air Batteries: Will They Be the Future Electrochemical Energy Storage Device of Choice? *ACS Energy Lett.* **2017**, *2*, 1370–1377.

(2) Li, Y.; Gong, M.; Liang, Y.; Feng, J.; Kim, J.-E.; Wang, H.; Hong, G.; Zhang, B.; Dai, H. Advanced Zinc-Air Batteries Based on High-Performance Hybrid Electrocatalysts. *Nat. Commun.* **2013**, *4*, 1805.

(3) Kim, B. G.; Kim, H.-J.; Back, S.; Nam, K. W.; Jung, Y.; Han, Y.-K.; Choi, J. W. Improved Reversibility in Lithium-Oxygen Battery: Understanding Elementary Reactions and Surface Charge Engineering of Metal Alloy Catalyst. *Sci. Rep.* **2015**, *4*, 4225.

(4) Han, X.; Zhang, W.; Ma, X.; Zhong, C.; Zhao, N.; Hu, W.; Deng, Y. Identifying the Activation of Bimetallic Sites in NiCo2S4@g-C3N4-CNT Hybrid Electrocatalysts for Synergistic Oxygen Reduction and Evolution. *Adv. Mater.* **2019**, *31*, 1808281.

(5) Han, X.; He, G.; He, Y.; Zhang, J.; Zheng, X.; Li, L.; Zhong, C.; Hu, W.; Deng, Y.; Ma, T.-Y. Engineering Catalytic Active Sites on Cobalt Oxide Surface for Enhanced Oxygen Electrocatalysis. *Adv. Energy Mater.* **2018**, *8*, 1702222.

(6)[°]Han, X.; Wu, X.; Zhong, C.; Deng, Y.; Zhao, N.; Hu, W. NiCo2S4 Nanocrystals Anchored on Nitrogen-Doped Carbon Nanotubes as a Highly Efficient Bifunctional Electrocatalyst for Rechargeable Zinc-Air Batteries. *Nano Energy* **201**7, *31*, 541–550.

(7) Han, X.; Ling, X.; Wang, Y.; Ma, T.; Zhong, C.; Hu, W.; Deng, Y. Generation of Nanoparticle, Atomic-Cluster, and Single-Atom Cobalt Catalysts from Zeolitic Imidazole Frameworks by Spatial Isolation and Their Use in Zinc-Air Batteries. *Angew. Chem., Int. Ed.* **2019**, *58*, 5359–5364.

(8) Bu, Y.; Gwon, O.; Nam, G.; Jang, H.; Kim, S.; Zhong, Q.; Cho, J.; Kim, G. A Highly Efficient and Robust Cation Ordered Perovskite Oxide as a Bifunctional Catalyst for Rechargeable Zinc-Air Batteries. *ACS Nano* **2017**, *11*, 11594–11601.

(9) Ryu, J.; Jang, H.; Park, J.; Yoo, Y.; Park, M.; Cho, J. Seed-Mediated Atomic-Scale Reconstruction of Silver Manganate Nanoplates for Oxygen Reduction towards High-Energy Aluminum-Air Flow Batteries. *Nat. Commun.* **2018**, *9*, 3715. (10) Li, J.; Zhou, N.; Song, J.; Fu, L.; Yan, J.; Tang, Y.; Wang, H. Cu–MOF-Derived Cu/Cu2O Nanoparticles and CuNxCy Species to Boost Oxygen Reduction Activity of Ketjenblack Carbon in Al–Air Battery. *ACS Sustainable Chem. Eng.* **2018**, *6*, 413–421.

(11) Hwang, J.; Rao, R. R.; Giordano, L.; Katayama, Y.; Yu, Y.; Shao-Horn, Y. Perovskites in Catalysis and Electrocatalysis. *Science* **2017**, 358, 751–756.

(12) Liu, Q.; Yang, T.; Du, C.; Tang, Y.; Sun, Y.; Jia, P.; Chen, J.; Ye, H.; Shen, T.; Peng, Q. J. N. l.; et al. *In Situ* Imaging the Oxygen Reduction Reactions of Solid State Na–O2 Batteries with CuO Nanowires as the Air Cathode. *Nano Lett.* **2018**, *18*, 3723–3730.

(13) Yang, L.-P.; Mi, J.-L.; Liang, J.-H.; Zu, Z.-Y.; Zhang, P. J. A. A. E. M. Copper-Carbon: An Efficient Catalyst for Oxygen Reduction. ACS Appl. *Energy Mater.* **2019**, *2*, 6295-6301.

(14) Cui, L.; Cui, L.; Li, Z.; Zhang, J.; Wang, H.; Lu, S.; Xiang, Y. A Copper Single-Atom Catalyst towards Efficient and Durable Oxygen Reduction for Fuel Cells. *J. Mater. Chem. A* **2019**, *7*, 16690–16695.

(15) Wei, W.; Chen, W. Size-Dependent Catalytic Activity of Copper Nanoclusters for Oxygen Electroreduction in Alkaline Solution. Int. J. Smart Nano Mater. 2013, 4, 62–71.

(16) Wang, J.; Wang, K.; Wang, F.-B.; Xia, X.-H. J. N. c. Bioinspired Copper Catalyst Effective for Both Reduction and Evolution of Oxygen. *Nat. Commun.* **2014**, *5*, 1–9.

(17) Liu, K. Nanostructured Materials as Effective Catalysts for Oxygen Reduction Reactions (ORR). Doctoral Thesis, UC Santa Cruz, United States, 2015.

(18) Luo, L.; Liu, B.; Song, S.; Xu, W.; Zhang, J.-G.; Wang, C. Revealing the Reaction Mechanisms of Li-O2 Batteries Using Environmental Transmission Electron Microscopy. *Nat. Nanotechnol.* **2017**, *12*, 535-539.

(19) Zhu, Z.; Kushima, A.; Yin, Z.; Qi, L.; Amine, K.; Lu, J.; Li, J. Anion-Redox Nanolithia Cathodes for Li-Ion Batteries. *Nat. Energy* **2016**, *1*, 1–7.

(20) Yadegari, H.; Franko, C. J.; Banis, M. N.; Sun, Q.; Li, R.; Goward, G. R.; Sun, X. How to Control the Discharge Products in Na–O2 Cells: Direct Evidence toward the Role of Functional Groups at the Air Electrode Surface. *J. Phys. Chem. Lett.* **201***7*, *8*, 4794–4800.

(21) Yadegari, H.; Sun, Q.; Sun, X. Sodium-Oxygen Batteries: A Comparative Review from Chemical and Electrochemical Fundamentals to Future Perspective. *Adv. Mater.* **2016**, *28*, 7065–7093.

(22) Kang, S.; Mo, Y.; Ong, S. P.; Ceder, G. Nanoscale Stabilization of Sodium Oxides: Implications for Na–O2 Batteries. *Nano Lett.* **2014**, *14*, 1016–1020.

(23) Banis, M. N.; Yadegari, H.; Sun, Q.; Regier, T.; Boyko, T.; Zhou, J.; Yiu, Y. M.; Li, R.; Hu, Y.; Sham, T. K.; Sun, X. Revealing the Charge/Discharge Mechanism of Na–O2 Cells by *In Situ* Soft X-Ray Absorption Spectroscopy. *Energy Environ. Sci.* **2018**, *11*, 2073–2077.

(24) Sun, Q.; Lin, X.; Yadegari, H.; Xiao, W.; Zhao, Y.; Adair, K. R.; Li, R.; Sun, X. Aligning the Binder Effect on Sodium–Air Batteries. *J. Mater. Chem. A* **2018**, *6*, 1473–1484.

(25) Lin, X.; Sun, Q.; Yadegari, H.; Yang, X.; Zhao, Y.; Wang, C.; Liang, J.; Koo, A.; Li, R.; Sun, X. On the Cycling Performance of Na-O2 Cells: Revealing the Impact of the Superoxide Crossover toward the Metallic Na Electrode. *Adv. Funct. Mater.* **2018**, *28*, 1801904.

(26) Liu, Q.; Yang, T.; Du, C.; Tang, Y.; Sun, Y.; Jia, P.; Chen, J.; Ye, H.; Shen, T.; Peng, Q.; Zhang, L.; Huang, J. *In Situ* Imaging the Oxygen Reduction Reactions of Solid State Na–O2 Batteries with CuO Nanowires as the Air Cathode. *Nano Lett.* **2018**, *18*, 3723–3730.

(27) Liu, Q.; Geng, L.; Yang, T.; Tang, Y.; Jia, P.; Li, Y.; Li, H.; Shen, T.; Zhang, L.; Huang, J. *In Situ* Imaging Electrocatalysis in a Na-O2 Battery with Au-Coated MnO2 Nanowires Air Cathode. *Energy Storage Materials* **2019**, *19*, 48–55.

(28) Lutz, L.; Dachraoui, W.; Demortière, A.; Johnson, L. R.; Bruce, P. G.; Grimaud, A.; Tarascon, J.-M. Operando Monitoring of the Solution-Mediated Discharge and Charge Processes in a Na-O2 Battery Using Liquid-Electrochemical Transmission Electron Microscopy. *Nano Lett.* **2018**, *18*, 1280–1289.

(29) Kwak, W.-J.; Luo, L.; Jung, H.-G.; Wang, C.; Sun, Y.-K. Revealing the Reaction Mechanism of Na-O2 Batteries Using Environmental Transmission Electron Microscopy. *ACS Energy Lett.* **2018**, *3*, 393–399.

(30) Han, S.; Wang, J.; Shi, X.; Guo, M.; Wang, H.; Wang, C.; Gu, M. Morphology-Controlled Discharge Profile and Reversible Cu Extrusion and Dissolution in Biomimetic CuS. *ACS Appl. Mater. Interfaces* **2018**, *10*, 41458–41464.

(31) Araujo, R. B.; Chakraborty, S.; Ahuja, R. Unveiling the Charge Migration Mechanism in Na2O2: Implications for Sodium–Air Batteries. *Phys. Chem. Chem. Phys.* **2015**, *17*, 8203–8209.

(32) Carter, G. F.; Templeton, D. H. Polymorphism of Sodium Superoxide. J. Am. Chem. Soc. 1953, 75, 5247-5249.

(33) Zemann, J.; Wyckoff, R. W. G. Crystal Structures, 2nd ed. Acta Crystallogr. 1965, 1, 139.

(34) Zintl, E.; Harder, A.; Dauth, B. Gitterstruktur der Oxyde, Sulfide, Selenide und Telluride des Lithiums, Natriums und Kaliums. Zeitschrift für Elektrochemie und angewandte physikalische Chemie **1934**, 40, 588–593.

(35) McCloskey, B. D.; Garcia, J. M.; Luntz, A. C. Chemical and Electrochemical Differences in Nonaqueous Li–O2 and Na–O2 Batteries. *J. Phys. Chem. Lett.* **2014**, *5*, 1230–1235.

(36) Bender, C. L.; Schröder, D.; Pinedo, R.; Adelhelm, P.; Janek, J. One- or Two-Electron Transfer? The Ambiguous Nature of the Discharge Products in Sodium–Oxygen Batteries. *Angew. Chem., Int. Ed.* **2016**, *55*, 4640–4649.

(37) Liu, W.-M.; Yin, W.-W.; Ding, F.; Sang, L.; Fu, Z.-W. NiCo2O4 Nanosheets Supported on Ni Foam for Rechargeable Nonaqueous Sodium–Air Batteries. *Electrochem. Commun.* **2014**, *45*, 87–90.

(38) Hu, Y.; Han, X.; Zhao, Q.; Du, J.; Cheng, F.; Chen, J. Porous Perovskite Calcium–Manganese Oxide Microspheres as an Efficient Catalyst for Rechargeable Sodium–Oxygen Batteries. *J. Mater. Chem. A* 2015, 3, 3320–3324.

(39) Yin, W.-W.; Shadike, Z.; Yang, Y.; Ding, F.; Sang, L.; Li, H.; Fu, Z.-W. A Long-Life Na–Air Battery Based on a Soluble NaI Catalyst. *Chem. Commun.* **2015**, *51*, 2324–2327.