

Revealing the Reaction Mechanism of Na–O₂ Batteries using Environmental Transmission Electron Microscopy

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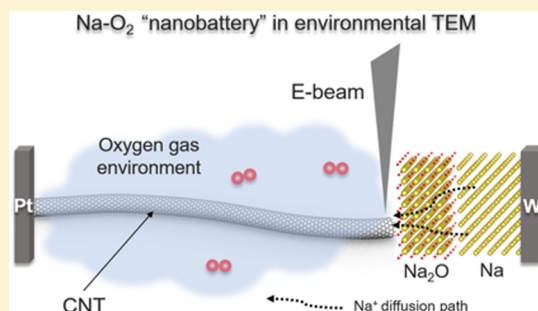
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Supporting Information

ABSTRACT: Sodium–oxygen (Na–O₂) batteries are being extensively studied because of their higher energy efficiency compared to that of lithium oxygen (Li–O₂) batteries. The critical challenges in the development of Na–O₂ batteries include the elucidation of the reaction mechanism, reaction products, and the structural and chemical evolution of the reaction products and their correlation with battery performance. For the first time, in situ transmission electron microscopy was employed to probe the reaction mechanism and structural evolution of the discharge products in Na–O₂ batteries. The discharge product was featured by the formation of both cubic and conformal NaO₂. It was noticed that the impingement of the reaction product (NaO₂) led to particle coarsening through coalescence. We investigated the stability of the discharge product and observed that the reaction product NaO₂ was stable in the case of the solid electrolyte. The present work provides unprecedented insight into the development of Na–O₂ batteries.



Research on alkali metal–oxygen batteries has been actively conducted for about a decade because of their theoretically high energy densities, which are higher than the maximum energy density limit of conventional lithium ion batteries.^{1–5} Among them, lithium–oxygen (Li–O₂) batteries, which theoretically have the highest energy density, have attracted the interest of many researchers.^{1–3} However, there are chronic problems in the Li–O₂ batteries related to solid Li₂O₂ discharge product formed on the air electrode. Surface passivation and pore clogging of the electrode due to the poor conductive character and irreversible decomposition of Li₂O₂ when charged with a huge overpotential cause parasitic side reactions. This results in the limitation of capacity, extremely low energy efficiency, and a poor cycle life for the Li–O₂ batteries.^{1–3,6,7} Studies on the efficient decomposition of Li₂O₂ by applying solid and liquid catalysts are being actively carried out,^{8–12} but there are problems associated with the secondary side reaction involving catalysts, which need to be solved with clear clarification of phenomena.^{9,13,14}

Sodium–oxygen (Na–O₂) batteries are being used as substitutes for Li–O₂ batteries since the Adelhelm group presented the small overpotential (<200 mV) of Na–O₂

batteries based on the formation and decomposition reaction of sodium superoxide (NaO₂).⁴ Theoretical and experimental data in previous papers have proved the facile decomposition of NaO₂ (the main discharge product) during charging compared to Li₂O₂.^{15–17} On the other hand, parasitic side reaction of NaO₂ with electrolyte was raised as a critical problem.^{18–20} Na₂O₂ (Na₂O₂·2H₂O)^{18,21} and Na_{2–x}O₂^{22,23} are also identified as other discharge products. Moreover, fundamental mechanistic studies for the drastic side reactions and various reaction products are rare because many variables and test conditions could affect the discharge products.^{20–28}

Therefore, studies for the elucidation of discharge product behaviors during operation are urgently needed. Although many reliable analytical results have been reported,^{24,28–30} they lack direct and in situ methods to reveal the entire process (discharge, rest, and charge), unlike with Li–O₂ batteries.^{31–33}

Herein, we performed in situ transmission electron microscopy (TEM) analysis for Na–O₂ batteries with

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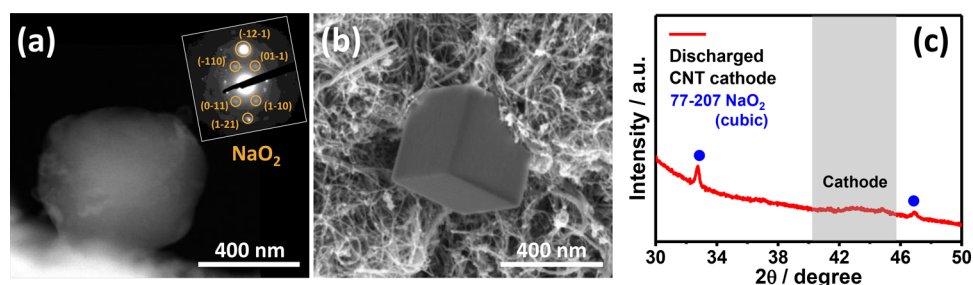


Figure 1. Identification of discharge products in solid-state Na–O₂ “nanobattery” compared to typical Na–O₂ batteries. (a) STEM image of NaO₂ discharge product on discharged CNT cathode in solid-state Na–O₂ nanobattery. (b) SEM image and (c) XRD pattern of cubic structural NaO₂ discharge product in typical Na–O₂ batteries using CNT cathode. Inset of panel a is the SAED pattern of the discharge product, which exhibited NaO₂ phase with only a few grains.

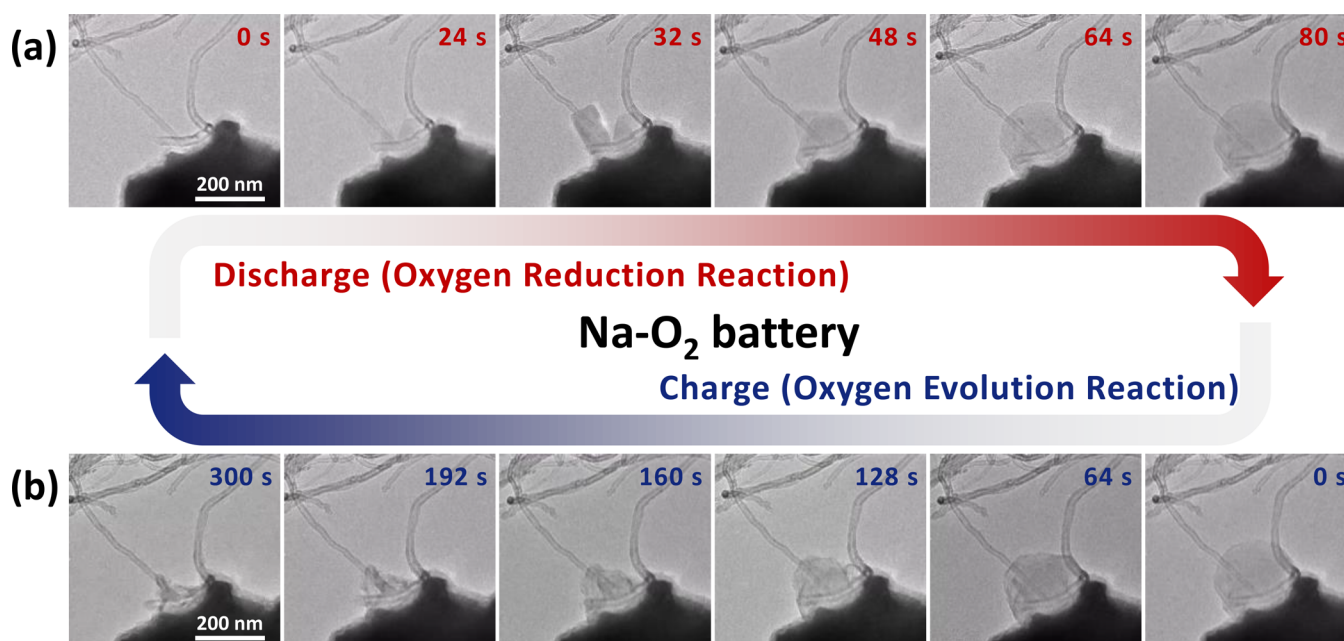


Figure 2. In situ observation of the morphological evolution of the discharge–charge product using a Na–O₂ nanobattery in an environmental TEM chamber. (a) The time-resolved TEM images depict the morphological evolution of the discharge product (ORR), which features the nucleation and growth of a cubic nanostructure. (b) The images depict the morphological evolution upon charging (OER), which features collapse of the reaction product.

aberration-corrected environmental TEM to understand the structural and phase evolution (formation, decomposition, and deterioration) of discharge products during discharge and charge, which has not yet been reported. In this work, a solid-state Na–O₂ nanobattery was constructed with a carbon nanotube (CNT) cathode, Na metal anode, and Na₂O solid electrolyte, which was formed on the surface of Na metal for in situ TEM analysis (Figure S1). This is the method reported previously for Li–O₂ batteries.³¹

To assess the suitability of a nanobattery as reference for elucidating the reaction mechanism, we compared the discharge product of the solid-state Na–O₂ nanobattery and typical Na–O₂ batteries using liquid electrolytes, before in situ observations using the solid-state Na–O₂ nanobattery. The scanning transmission electron microscopy (STEM) image in Figure 1a exhibits the solid bulk particle on the CNT cathode in the solid-state Na–O₂ nanobattery as discharge product, which was identified as NaO₂ from its selected area electron diffraction (SAED) pattern (inset data of Figure 1a and Figure S2).

By comparison of cubic structural NaO₂ identified by SEM and XRD analysis in typical Na–O₂ batteries (Figures 1b and

1c),^{4,15–21} it was confirmed that both batteries had the same discharge product, NaO₂. Therefore, the nanobattery was used for in situ analysis in this work to understand the mechanism of actual Na–O₂ batteries with the same discharge product.

During discharging and charging of the solid-state Na–O₂ nanobattery, the formation and decomposition of the reaction product were monitored by a series of time-resolved scanning TEM images, as shown in Figure 2 and Supplementary Movie 1. On discharging (Figure 2a), the formation and growth of the discharge product (which was typically NaO₂), which had bulk crystal structure, was confirmed. Through our in situ TEM analysis, it was demonstrated that the discharging process did not occur only through increasing the size of the discharge product. The morphological evolution of in situ TEM images from 24 to 48 s shows the formation of perpendicular pillar materials and their agglomeration during discharge, which helps more definitive demonstration of the formation of NaO₂. The agglomeration of small particles of discharge products leads to the formation of large NaO₂ particles (Figure S3 and Supplementary Movie 2). This observation presents an alternative way to grow the micrometer size of discharge

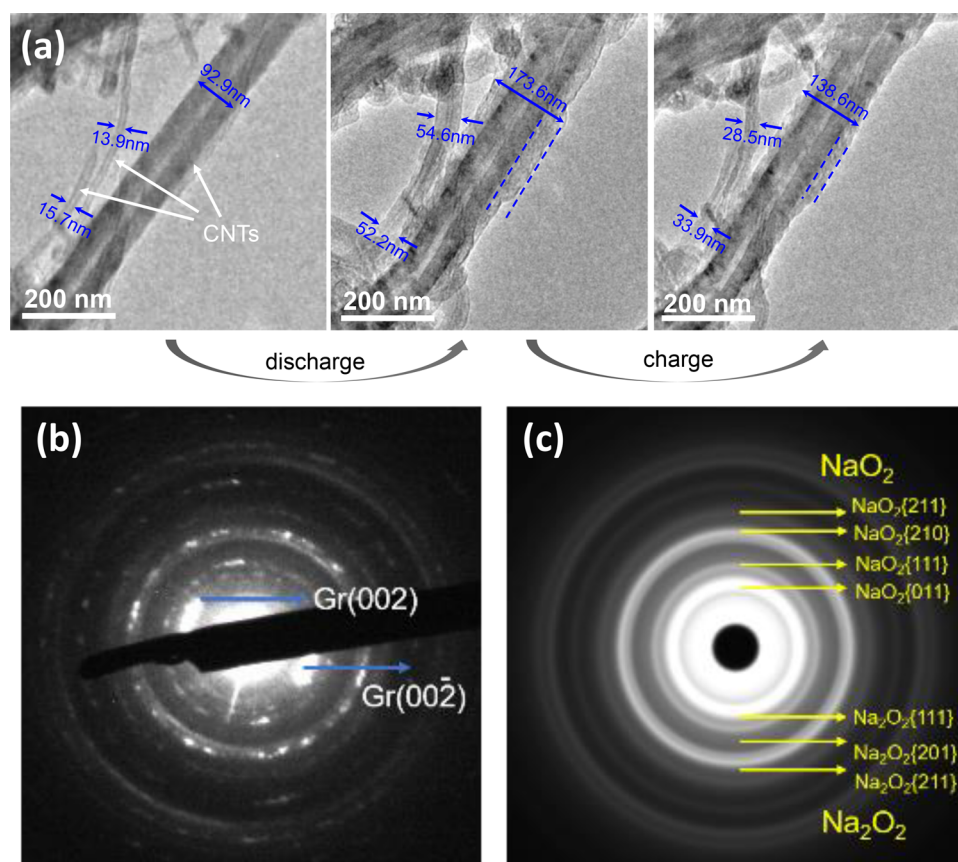


Figure 3. (a) In situ observation of the formation–decomposition of discharge products on CNT cathode surfaces upon discharge–charge. (b) SAED pattern for phase identification of remnants on the surface of CNTs. (c) Processed SAED pattern identifying both NaO₂ and Na₂O₂ phases in conformal coatings of discharge product. Enlarged SAED pattern with phase identification is supplied in Figure S7. Note the diffraction spots labeled as Gr(002) and Gr(002̄) are from the CNTs.

product beside the commonly known method of solution precipitation in liquid electrolyte.

Unlike hollow spherical Li₂O₂ particles in Li–O₂ batteries,^{1–3} the discharge product of Na–O₂ batteries was not hollow, but a bulk structure which was confirmed by high-angle annular dark-field (HAADF) STEM observation (Figure S4). The formation reaction of NaO₂ did not involve the disproportionation reaction which evolves O₂ gas and inflates the reaction product as in previous data on the Li–O₂ nanobattery.³¹

On charging (Figure 2b), decomposition and shrinkage of the discharge product were confirmed. The surface of the discharge product that was in contact with the CNT cathode shrank first. After a certain level, no further decomposition occurred and the remnant remained on the electrode surface. In other words, larger NaO₂ particles decomposed upon charging, but the film layers formed on the surfaces of CNTs were not completely removed upon charging.

On second discharge, the formation and growth of bulk crystal NaO₂ was confirmed (Figure S5). The difference between the discharged cathode at the first cycle and the second cycle was the irreversible remnant on the electrode surface.

To understand the irreversible product on the surface of electrode, the remnant on the electrode surface was analyzed. As shown in Figure 3a, the film-type product grew on the surface of the CNT cathode during discharge, but it could not be completely removed upon charging (Supplementary Movie

3) and become the remnant on the electrode surface, unlike large cubic NaO₂. It is noted that bare CNTs deposited ~40 nm coating of discharge product, but after the charge process, only half of this thickness was decomposed, as shown in Figure 3a.

The irreversible remnants on the electrode surface (shown in Figure 3a) during cycling test were identified as NaO₂ + Na₂O₂ from the SAED patterns (Figures 3b,c and S7). This irreversible mixture of NaO₂ + Na₂O₂ led to increasing overpotential during charge.^{18–23}

We further interrogated the intrinsic stability of the as-formed discharge product by terminating the reaction and keeping the discharge product under the vacuum environment inside the TEM for a prolonged time. This is vital to elucidate the deterioration of NaO₂ by chemical side reaction with liquid electrolyte in typical Na–O₂ batteries,^{18–20} because the chemical side reaction between NaO₂ and electrolyte solvent was absent here because of the “all-solid” nature of the nanobattery, which uses the solid-state Na₂O as the electrolyte.

As shown in Figure 4a, we monitored two major types of discharge products: (I) large cubic particles and (II) conformal coatings. Immediately after their formation, the large cubic particles displayed NaO₂ (*Fm3m*) phase, as shown in Figure 4b (left, experimental; right, simulated SAED patterns). After 8 h of staging in vacuum environment, the major phase remained NaO₂ (*Fm3m*), but some small additional particles were formed as NaO₂ (*Pnmm*), as seen in Figure 4d. The phase transition happened on the surface of the cubic particle, as seen as some

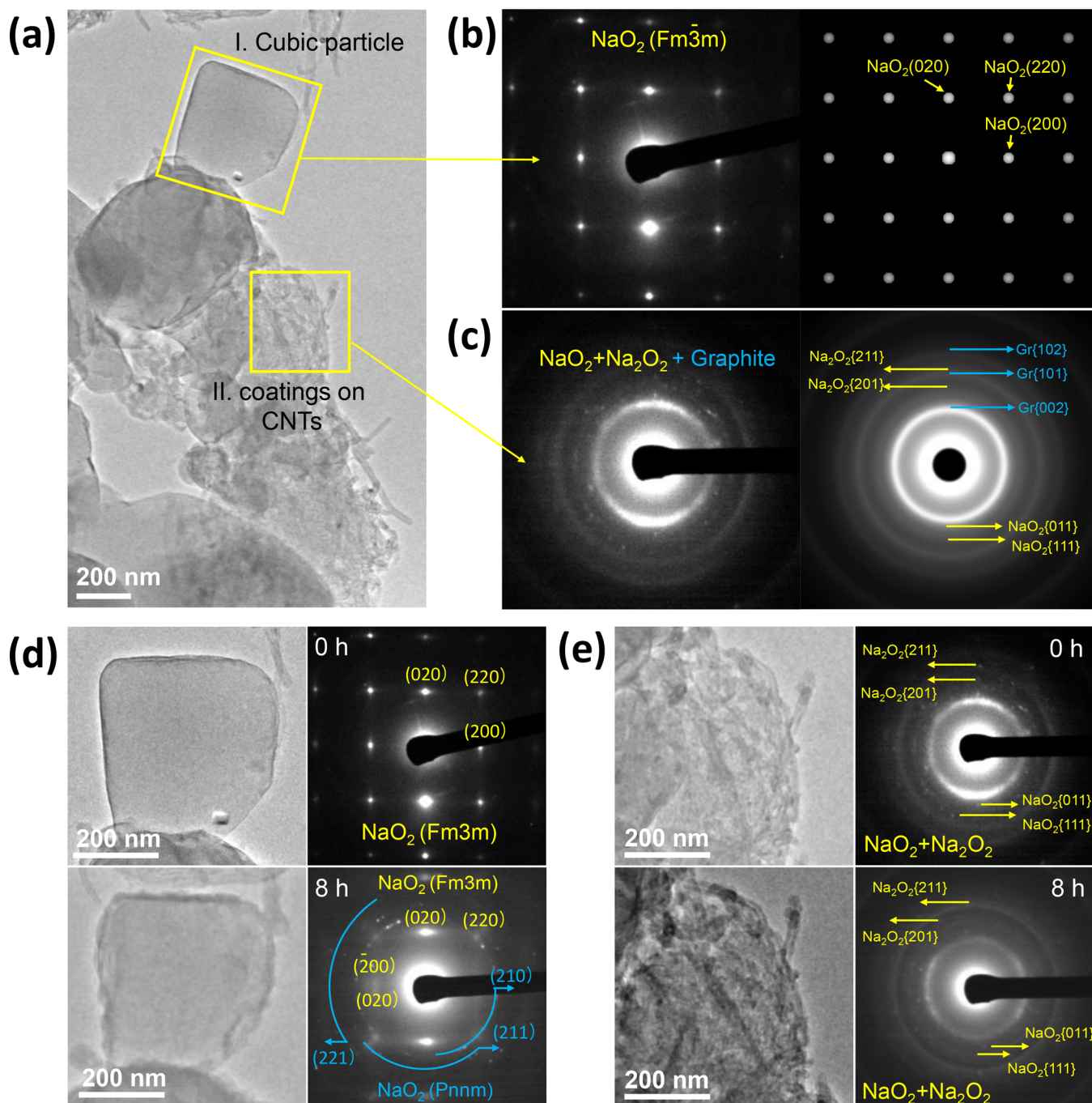


Figure 4. In situ observation of the stability of the discharge product (NaO_2) for elongated time. (a) As-formed (I) large cubic NaO_2 particle and (II) conformational coatings on CNTs. (b and c) Their initial phases are identified as NaO_2 ($Fm\bar{3}m$) and $\text{NaO}_2 + \text{Na}_2\text{O}_2$. (d) Comparison of the phase of large cubic NaO_2 after 8 h. The major phase of NaO_2 ($Fm\bar{3}m$) remained unchanged, but a minor NaO_2 ($Fm\bar{3}m$) to NaO_2 ($Pnmm$) transition occurred at the surface of the particle (shown as the rough surface of the cubic particle in the lower panel). (e) Comparison of the phase of conformational coating on CNTs confirmed no observable change for the mixture $\text{NaO}_2 + \text{Na}_2\text{O}_2$.

“roughed” surface after 8 h (lower panel of Figure 4d). Figures 4c,e and S8 show the phase of conformational coatings on CNTs, which remained as $\text{NaO}_2 + \text{Na}_2\text{O}_2$ mixture during the 8 h staging process.

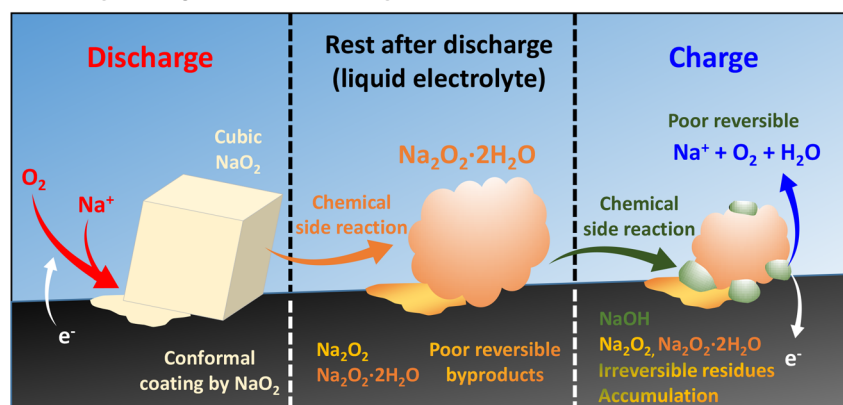
This result proves the intrinsic stability of the major discharge product $\sim\text{NaO}_2$ in the system with no contact to the liquid electrolyte, i.e., NaO_2 does not easily go through disproportionation reaction as LiO_2 and remains stable for at least 8 h. Previous work reported^{18–23} when using liquid electrolytes, time-dependently, NaO_2 changed to $\text{Na}_2\text{O}_2 \cdot 2\text{H}_2\text{O}$

because of chemical reactions triggered by the dissolution and ionization of NaO_2 in the liquid electrolyte, as illustrated in Scheme 1a.

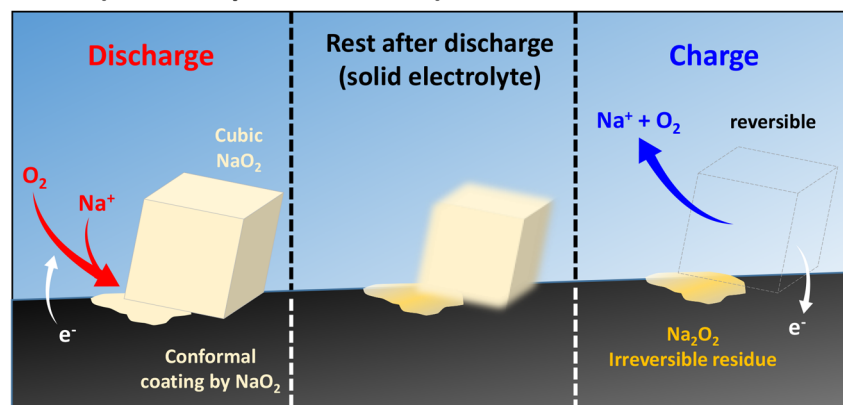
Our results suggest this phase change may be due to the side reaction between the liquid electrolyte and NaO_2 , although the NaO_2 itself is stable. It indicates that solid electrolyte (e.g., NASICON) is helpful for the stabilization of NaO_2 , as prolonged discharge products to prevent chemical changes associated with liquid electrolyte. However, to avoid extremely large overpotential, the sluggish kinetics of solid electrolytes

Scheme 1. Proposed Reaction Mechanism of the Na–O₂ Batteries (a) with or (b) without the Side Reaction Related to the Proton Sources (Solvent Decomposition or Water Impurity)

(a) Na–O₂ batteries using liquid electrolyte
(with proton source)



(b) Na–O₂ batteries using solid electrolyte
(without proton source)



should be of concern, and further studies are necessary. It is also noted that while large cubic NaO₂ particles were reversibly formed and decomposed, conformational coatings with a mixture of NaO₂ + Na₂O₂ on the CNT surfaces maintained the phase throughout the process, which was a potential issue for the cyclability of the battery (Scheme 1b).

In summary, in situ TEM studies revealed the reaction pathway and morphological evolution of Na–O₂ batteries, featuring the formation of NaO₂ in both cubic and conformational coating film forms during the discharge and charge cycles of the Na–O₂ batteries. For the first time, it has been noticed that the impingement of reaction product (NaO₂) can lead to the coarsening of the particle through coalescence. The irreversible residues formed on the electrode surface during charging were identified as a mixture of NaO₂ and Na₂O₂. The chemical side reaction between NaO₂ and electrolyte is absent when the solid electrolyte was used instead of the liquid electrolyte. These observations provided insights into optimized design of Na–O₂ chemistry for improved battery performance.

■ ASSOCIATED CONTENT

📄 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsenerylett.7b01273.

Experimental procedures and methods, diffraction patterns of discharge products, time-resolved TEM data for the evolution of discharge product on second discharge, beam blank experiment for checking side effects of beam on discharge product (PDF)

In situ observation of the morphological evolution of the discharge–charge product of the Na–O₂ nanobattery in an environmental TEM chamber (AVI)

In situ observation of the growth of NaO₂ crystals upon discharge (AVI)

In situ observation of the decomposition of discharge products on CNTs cathodes upon charging; decomposition of conformational coating on CNTs upon charging (AVI)

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Notes

The authors declare no competing financial interest.

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