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From K-O₂ to K-Air Batteries: Realizing Superoxide Batteries on the Basis of Dry Ambient Air

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Supporting information for this article is given via a link at the end of the document.

Abstract: Superoxide-based potassium-oxygen (K-O₂) batteries have demonstrated enormous potential to realize high-energy-density battery chemistry with low round-trip overpotentials. Although using air cathode is the ultimate goal to unlock the full potential of superoxide batteries, prior studies were limited to pure oxygen. Herein, we report the first K-air (dry) battery based on reversible superoxide electrochemistry. Spectroscopic and gas chromatography analyses are applied to evaluate the reactivity of KO₂ in ambient air. Despite that KO₂ reacts with water vapor and CO₂ to form KHCO₃, it is found to be highly stable in dry air. With this knowledge, rechargeable K-air (dry) batteries were successfully demonstrated by employing dry air cathode. We further prove that the reduced partial pressure of oxygen plays a critical role in boosting the battery lifespan. With a more stable environment for K anode, a K-air (dry) battery delivers over 100 cycles (> 500 hours) with low round-trip overpotentials and high coulombic efficiencies as opposed to traditional K-O₂ battery that fails at an early stage. This work sheds light on the benefits and restrictions of employing air cathode in superoxide-based batteries, and will be of use for the development of practical metal-air batteries.

Non-aqueous alkali metal-air batteries are deemed as energy storage alternatives to the current lithium-ion batteries due to their large energy densities and low costs.^[1] To date, these gas-open systems have been largely limited to pure oxygen (O₂) conditions due to the cell contamination and degradation caused by unwanted atmospheric components, including nitrogen, carbon dioxide (CO₂), and moisture. In order to eliminate additional needs for the air purification device and O₂ cylinder, it is crucial to design a practical metal-air battery operating in ambient air.

A few groups have investigated the chemistry of metal-O₂ batteries in an air-like atmosphere. Note that CO₂ is an inevitable contaminant in metal-air batteries, which adversely affects the O₂ electrochemistry. Takechi et al. noticed that O₂ can be captured by CO₂ to form a series of intermediates (e.g., peroxy carbonate and peroxydicarbonate).^[2] The final product of Li₂CO₃ results in a sluggish decomposition kinetics and requires electrocatalysts to assist the removal of carbonate, leading to an intractable issue in metal-CO₂ batteries.^[3] Peng et al. revealed that the build-up of Li₂CO₃, by the reaction between LiO₂ intermediate and CO₂, is the Achilles' heel of lithium (Li)-air batteries.^[4] Zhou et al. applied ionic liquid (IL)-based gel to prevent electrolyte degradation when operating in ambient air.^[5] Nevertheless, Li₂CO₃ still accumulates and undermines the reversibility of Li-O₂ electrochemistry. Curtiss and Salehi-Khojin et al. reported a long-life Li-O₂ battery based on IL-dimethyl sulfoxide electrolyte in an air-like

atmosphere with a large round-trip overpotential (1.3~1.62 V).^[6] Lately, similar studies have been brought to sodium (Na)-air electrochemistry. Sun et al. discovered that CO₂ and moisture dramatically alter the electrochemical pathway of Na-air batteries and promotes side products formation, including Na₂O₂·2H₂O, NaOH, and Na₂CO₃.^[7] The continuous accumulation of peroxide and carbonate largely limits the battery cyclability.^[8] Since the demonstration of potassium (K)-O₂ battery by our group in 2013, great progress has been made, including anode stability improvement, electrolyte formula optimization, and cathode design.^[9] One major advantage is that KO₂ is the only product in a K-O₂ battery without the interference of peroxide species.^[1b] Moreover, pure KO₂ is commercially available. This facilitates us to quantitatively investigate its reactions with moisture/CO₂ and understand the role of these reactions in a K-air (dry) battery.

Herein, our work explores for the first time the highly reversible KO₂ electrochemistry under dry ambient air. The K-air (dry) battery delivers a small round-trip overpotential of 74 mV and offers a flat discharge voltage output at 2.40 V (vs. K⁺/K). Based on chemical quantifications and spectroscopic characterizations, the superoxide chemistry is identified as the reaction mechanism and such reaction route is barely affected by air components (especially CO₂) in the absence of moisture. As a result, over 100 cycles (above 500 hours) with a high coulombic efficiency (CE) of 99.0% have been achieved. In the light of the feasibility of utilizing dry ambient air and the realization of superb reaction kinetics with an impressive battery lifespan, the "open" K-air (dry) battery demonstrated here motivates the development of superoxide batteries as a promising high-energy-density alternative to current lithium-ion batteries technology.

To explore the effects of different gas components, the reactivity of KO₂ was first examined by aging the commercial KO₂ powder in air-tight vials filled with dry CO₂, wet CO₂ (namely CO₂ saturated with water vapor), dry air, and dry O₂, respectively (Supporting Information, **Figure S1a-c**). The yellow KO₂ powder turns to white only in wet CO₂ within 24 hours, while no obvious color change is observed in other vials. As shown in X-ray diffraction (XRD) patterns, the white product is identified as KHCO₃ (JCPDS No. 12-0292) in wet CO₂, while the KO₂ (JCPDS No. 43-1020) does not change in other atmospheres (Supporting Information, **Figure S1d**). Raman spectrum further confirms the dominant KO₂ (1142 cm⁻¹) in dry CO₂ (same as dry O₂ and dry air), while only KHCO₃ is present in wet CO₂ (Supporting Information, **Figure S1e**). Therefore, the presence of water vapor is critical for CO₂ to react with KO₂. It is also revealed that the KO₂ powder is highly sensitive to the moisture in ambient air (relative humidity of

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~30%), and the final byproducts are identified as carbonate and hydrated hydroxide after aging (Supporting Information, **Figure S2**).

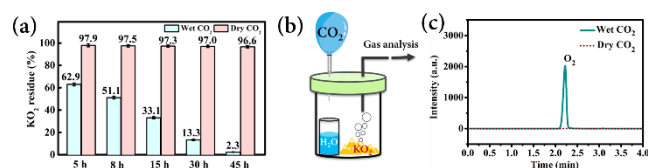
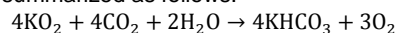


Figure 1. Stability test of commercial KO₂ powder. (a) Amounts for residual KO₂ in dry/wet CO₂ based on 3 parallel titrations. (b) Schematic illustration of the gas-analysis process. (c) Gas evolution from aged KO₂ powder in dry/wet CO₂ for 72 hours. Commercial KO₂ powder was put inside an air-tight vial, which is connected to a balloon filled with high-purity CO₂. A smaller vial with deionized water provides moisture with a relative humidity of 100% if necessary. The evolved gas was analyzed by gas chromatography with N₂ as the carrier gas.

To conduct a quantitative analysis on the detrimental effect of CO₂ on the KO₂ stability, a specific amount of KO₂ powder (~10 mg) was placed in both dry CO₂ and wet CO₂ atmospheres for comparison. The amount of KO₂ residue was determined by UV-vis spectroscopy following its reaction with TiO(SO₄) aqueous solution (Supporting Information, **Figure S3**). It is found that most KO₂ (96.6 wt%) is left in dry CO₂, while there is only 2.3 wt% KO₂ that remains in wet CO₂ after 45 hours (**Figure 1a**). Gas chromatography (GC) measurement was carried out to investigate possible gas evolution (**Figure 1b**). No O₂ signal is observed in dry CO₂, confirming the superb chemical stability of KO₂ (**Figure 1c**). In stark contrast, the significant O₂ signal is identified in wet CO₂. Through the spectroscopic and GC analysis on the formed product, the side reactions between KO₂ and wet CO₂ can be summarized as follows:



Given substantial water vapor in ambient air, the aforementioned side reaction can easily take place in a K-air (dry) electrochemical cell and produce KHCO₃ as discharge products together with O₂ evolution.

As a proof of concept, a K-air (dry) battery consisting of metallic K anode and dry air cathode was assembled. The conventional carbon paper was used as the gas diffusion layer, and a moisture trap was needed to remove the water from the air cylinder. The cyclic stability of K-air (dry) batteries was evaluated with shallow cycling (capacity of 0.5 mAh at the rate of 0.2 mA). Without employing the O₂ shield membrane or solid electrolyte, the K-air (dry) battery is demonstrated to deliver over 100 stable cycles (above 500 hours) with a low round-trip overpotential of 74 mV and a high average CE of 99.0% (**Figure 2a-b**). When cycled with different depths of discharge (DODs) of 1, 2, and 3.92 mAh, highly reversible charge processes can still be achieved (CEs%: 98.9%-99.3%) with merely 110 mV round-trip overpotential (energy efficiencies%: 94.2%-96.1%) (**Figure 2c**). The XRD pattern confirms that the discharge product is still crystalline KO₂ in a K-air (dry) battery and these KO₂ crystals would disappear after charge, suggesting that the various components in dry air do not alter the essential superoxide-based electrochemistry of batteries (**Figure 2d**). For experimentally studying the morphology change upon discharge/charge, a series of K-air (dry) batteries were assembled and discharged to 1 and 2 mAh (Supporting Information, **Figure S4**). Scanning electron microscopy (SEM) images of the discharge cathode reveal that the cubic-shaped KO₂ crystals are formed on the surface of

carbon paper cathode. These KO₂ crystals exhibit a similar cubic morphology just as that formed in K-O₂ batteries.^[9] The area density of KO₂ crystals increases at a higher DOD. After charging to 1 mAh, the cubic KO₂ crystals exhibit a volume shrinkage. When the cell is charged to 3.0 V, most cubes are removed and only a film-like residue is left on the surface. This is ascribed to the side products based on our prior study.^[10]

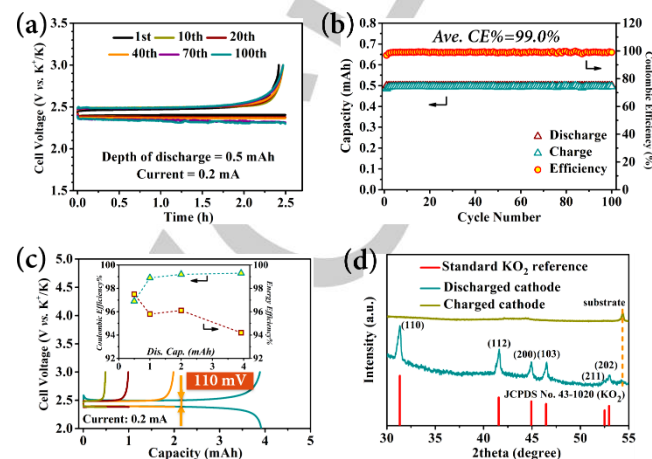


Figure 2. (a) Typical discharge-charge curves of K-air (dry) batteries. (b) Cycling performance and coulombic efficiency of K-air (dry) batteries (DOD = 0.5 mAh, *I* = 0.2 mA). (c) Voltage profiles of K-air (dry) batteries cycling at the current of 0.2 mA with different DODs (cycled between 2-3 V vs. K^{+/K}). The corresponding CEs (left) and energy efficiencies (right) are shown in the inset. (d) XRD pattern of the discharged cathode and charged cathode in K-air (dry) batteries (DOD = 1 mAh). The XRD peak at 54.4° is ascribed to the carbon paper substrate.

The voltage profile of a K-air (dry) battery is similar to a K-O₂ battery, except for the slightly lower voltage plateau (**Figure 3a**). Based on the Nernst equation, the potential is decreased by 40 mV due to the lower partial pressure of O₂ in the air (~1/5 by volume), which results in an equilibrium potential of 2.446 V. Cyclic stability of the K-air (dry) batteries is further compared with K-O₂ batteries in **Figure 3b**. A common K-O₂ battery using potassium hexafluorophosphate (KPF₆)/1,2-dimethoxyethane (DME) electrolyte exhibits sudden death after 40 cycles (~200 hours). With a shallow cycling capacity of 0.5 mAh, the K-O₂ battery sustains 35 stable cycles (Supporting Information, **Figure S5a-b**). Then its round-trip overpotential rapidly increases after the 35th cycle due to serious anode corrosion (**Figure 3c**). Finally, the pristine K metal anode turns to a yellow disc, and Raman spectrum reveals that the main components on the surface of cycled K are KO₂, KOH, and K₂CO₃, etc. (**Figure 3d**). Note that same byproduct components with relatively lower intensities are identified on the corroded K anode from K-air (dry) batteries.

To eliminate the influence of cathode degradation on battery performance, the K anode and separator were replaced and the electrolyte was refilled after the battery failure. The same battery soon recovers to show normal voltage curves after replacing the O₂-corroded K anode (Supporting Information, **Figure S5c-d**). The first charge curve (with dash line) shows a relatively larger capacity, likely due to the accumulation of undecomposed KO₂ in previous cycles. Based on the above observations, the anode degradation due to O₂ crossover is mainly responsible for the failure of K-O₂ batteries. A similar phenomenon is also observed in K-air (dry) batteries, which dies after the 120th cycle. The cell voltage and cycling completely recover with a new K anode

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(Supporting Information, **Figure S6**). A longer K anode lifetime is realized in a K-air (dry) battery owing to the lower O₂ permeation/crossover rate in air, which eventually contributes to the enhanced lifespan of K-air (dry) batteries. Details on the kinetics influence are subject to further investigation in the future.

To mimic the K anode corrosion under various gas components, a metallic K was placed in a DME solution saturated with dry CO₂, wet CO₂, dry air, and dry O₂, respectively. Raman and nuclear magnetic resonance (NMR) were adopted to analyze the aged K samples. **Figure S7a** (Supporting Information) shows that none of the aged samples remain shiny metal luster, white byproduct layers are found on the surface instead. Raman spectra confirm that the KOH component is formed on the K surface in O₂ and air environment, while K₂CO₃ is identified in dry CO₂ and wet CO₂ atmospheres (Supporting Information, **Figure S7b**). By dissolving in D₂O, the surface layer components were further characterized by NMR (Supporting Information, **Figure S8**). It is found that ¹H NMR shows peaks attributed to formate (HCOOK, δ = 8.44 ppm) in dry CO₂, and extra acetate (CH₃COOK, δ = 1.90 ppm) and dimethyl ether (CH₃OCH₃, δ = 3.20 ppm) are found on the aged K in wet CO₂.^[11] In comparison, none of the aforementioned components are detected (except for residual DME) on K surface in dry O₂ and air. Despite this, the parasitic reactions between K anode and the electrolyte/O₂ are much increased with more side products accumulation during long-term cycling (**Figure 3d**). An O₂-blocking membrane and a stable solid electrolyte interphase are critical to protect the K anode from O₂ crossover and electrolyte decomposition, and further boost the K-O₂/air (dry) batteries performance.

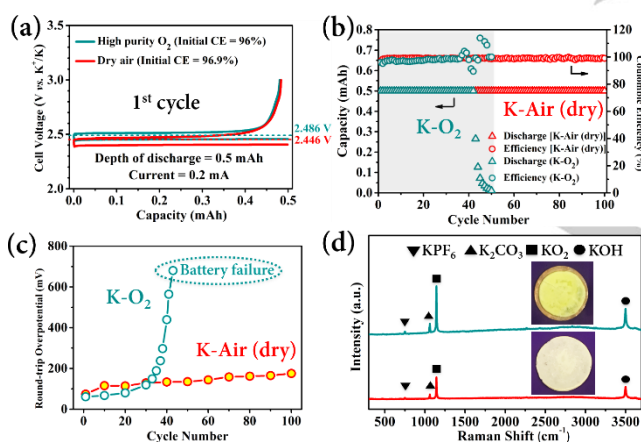


Figure 3. Comparison between K-O₂ and K-air (dry) batteries in (a) first voltage profiles, (b) cyclic stability, and (c) round-trip overpotentials. The round-trip overpotentials are estimated by measuring the middle potential in the discharge/charge processes. The batteries are tested at the same conditions (rate at 0.2 mA with the curtailed capacity at 0.5 mAh). (d) Raman spectrum of the corroded K in K-O₂ batteries (cyan) and K-air (dry) batteries (red) after 50 cycles. The inset shows the optical images of corroded K. The KPF₆ component comes from salt residue.

As shown in **Figure 2(a-b)** that the first cycle shows the lowest CE compared to other cycles. The titration method was then applied to quantify the reversible KO₂ amounts on the cathode in the first cycle (Supporting Information, **Figure S9a**). A K-air (dry) battery was first discharged to a DOD of 1 mAh, which is equal to 37.3 μmol electrons (Supporting Information, **Figure S9b**). From the Raman analysis, KO₂ dominates the discharge product on the air cathode (**Figure 4a**). X-ray photoelectron spectroscopy (XPS)

spectra of the cathode reveal a limited growth of carbonyl species and carbonate from decomposition after the first discharge (Supporting Information, **Figure S10a-b**). The formation of stable KO₂ without the interference of peroxide and other byproducts, as indicated by the Raman result (Supporting Information, **Figure S10c**), is crucial for improving the reversibility of KO₂-based superoxide batteries. Titration results reveal that 37.1 μmol KO₂ is formed (Supporting Information, **Table S1**). After charging to 3.0 V, Raman analysis confirms the disappearance of KO₂, and quantitative titration shows that some dead superoxide/peroxide is left in the air electrode that is equivalent to 0.7 μmol dead KO₂ and contributes to an irreversible capacity of 1.9%. We propose that this is due to KO₂ reacting with trace H₂O in the electrolyte by forming titratable KHO₂ (See the detailed analysis in Supporting Information, **Figure S11**). This indicates that a total amount of 37.1 μmol KO₂ forms during the discharge process, and 36.4 μmol is reversibly charged in the first cycle. In addition, high e⁻/KO₂ ratios of 1.02 and 1.01 are estimated for the O₂ reduction and evolution processes, respectively. Notably, a slight portion of KO₂ could still react with DME electrolyte and form non-titratable side products (e.g., formate, acetate, and methoxyacetate) on the surface, which account for another irreversible capacity portion (0.2 μmol, 0.5%). The related mechanism is discussed in our prior work.^[10] The detailed information on the different fractions of electrons during the first cycle is summarized in **Figure 4b**. 97.6% of electrons are reversible through KO₂ formation/decomposition in a K-air (dry) battery, while 2.4% loss of electrons is ascribed to the side reactions between KO₂ and electrolyte/H₂O, which consists of dead KO₂ (1.9%) and non-titratable side products (0.5%).

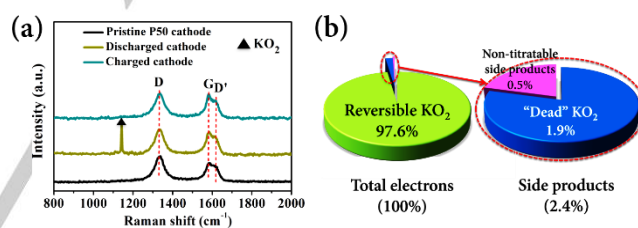


Figure 4. (a) Raman spectra of the pristine, discharged, and charged cathodes in K-air (dry) batteries. The typical Raman peaks related to carbon paper substrate are also labeled. (b) The fraction of total electrons (with 1 mAh capacity) attributed to the formation of reversible KO₂, "dead" KO₂, and non-titratable side products in the first cycle.

In summary, our study demonstrated for the first time a K-air (dry) battery on the basis of superoxide chemistry. The high reversibility of the O₂/KO₂ redox couple is well-maintained in the dry ambient air. Quantitative titration verifies the high-efficiency one-electron transfer processes in a K-air (dry) battery. Meanwhile, spectroscopic and GC analyses reveal that KO₂ does not react with dry CO₂. Considering the small amounts of CO₂ (0.04% in air) and H₂O (removed by moisture trap) in a K-air (dry) battery, pure O₂ is not required for KO₂-based superoxide batteries. As a result, the cost can be lowered and the gas-open K-air (dry) battery technology is practically feasible. Further Raman analysis determines that K anode corrosion (accumulation of side products) resulted from O₂ crossover is the main reason for K-O₂ battery failure. The reduced O₂ partial pressure benefits the lifetime of K anode, which accounts for the enhanced lifespan of K-air (dry) battery. At a controlled DOD (0.5 mAh), K-air (dry) batteries system demonstrates the reversible

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O₂/KO₂ conversion (with 74 mV round-trip overpotential), and a superb cycling (over 100 cycles) is achieved with a high CE of 99.0%. We hope these findings would facilitate a better understanding of superoxide chemistry and motivate the development of practical air cathode for superoxide battery technologies.

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Conflict of interest

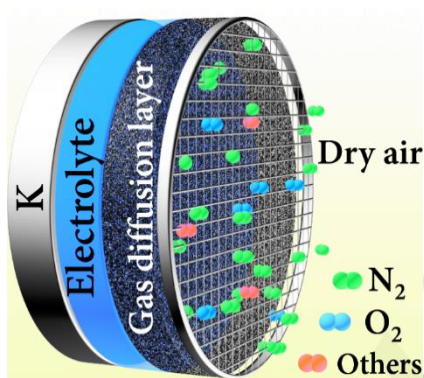
The authors declare no conflict of interest.

Keywords: air battery • anode degradation • oxygen crossover • potassium-oxygen batteries • superoxide chemistry

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Entry for the Table of Contents



Getting rid of O₂ cylinder: Dry ambient air is utilized for the first demonstration of K-air (dry) battery (see picture), which sheds light on the reversible potassium superoxide electrochemistry. This motivates the development of high-efficiency superoxide battery technology and represents an important step towards the direct use of air in metal-air batteries.