

Overcharge for Reviving Failed Li-O₂ Batteries

Kai Chen

Changchun Institute of Applied Chemistry

Dong-Yue Yang

Changchun Institute of Applied Chemistry

Jin Wang

Changchun Institute of Applied Chemistry

Gang Huang

Changchun Institute of Applied Chemistry <https://orcid.org/0000-0003-2518-8145>

xin-bo Zhang (✉ xbzhang@ciac.ac.cn)

Changchun Institute of Applied Chemistry <https://orcid.org/0000-0002-5806-159X>

Article

Keywords: batteries, Li-O₂ batteries, overcharge, battery life

Posted Date: August 31st, 2021

DOI: <https://doi.org/10.21203/rs.3.rs-823894/v1>

License:   This work is licensed under a Creative Commons Attribution 4.0 International License.

[Read Full License](#)

Abstract

Prolonging the lifetime of batteries is a long-term pursuit, and it is also one of the prerequisites for the practical application of batteries. However, this is really challenging for high-energy Li-O₂ batteries due to their poor charge efficiency and cathode passivation induced by products accumulation. Here, we demonstrate that overcharging the Li-O₂ batteries can facilitate the decomposition of residue products and thus revive the cathode, which allows further operation of Li-O₂ batteries for 1316 cycles. This long lifetime not only makes full use of the Li anode, but also enables the battery recycling in a safer way. Furthermore, applying anode protection and overcharge together, the life of batteries can be extended to a record high value of 2714 cycles. This overcharge strategy simplifies the cathode regenerating procedures, realizing system-level efficient use of battery components and prolonging the life of Li-O₂ batteries that can meet the requirements of practical applications.

Main Text

With a theoretical energy density ten times higher than current Li-ion batteries, Li-O₂ batteries have received intensive research in the past two decades. A typical Li-O₂ battery consists of a Li anode, an organic electrolyte, and a porous cathode, and follows the electrochemical reaction of $\text{Li}^+ + \text{O}_2 + \text{e}^- \leftrightarrow \text{Li}_2\text{O}_2$ with the formation and decomposition of Li₂O₂ during the discharge and charge processes. Though the reaction looks simple, there are several parasitic reactions happening during battery cycling, making the actual situation of the battery extremely complicated. Especially, the existence of superoxide intermediates, like O₂⁻ and LiO₂, during battery operation is aggressive towards both the cathodes and electrolytes. Moreover, the discharge product, Li₂O₂, is not completely compatible with the cathode and electrolyte, inducing the formation of carbonate films at each contact interface¹. The situation is even worse when considering the recently demonstrated singlet oxygen (¹O₂) rendered severe electrolyte decomposition². All these will cause parasitic reactions that generate hardly decomposed insulating side products on the cathode. The continuous accumulation of the side products as cycling goes on will bury the active sites and block the electron transfer, preventing the proceedings of the electrochemical reactions. In addition, besides the cathode, the Li anode also endures grievous corrosion by H₂O and intermediates with the generation of thick but porous LiOH layer. The degradation of the cathode and anode together limits the lifetime of Li-O₂ batteries, typically less than 300 cycles, which is far from meeting the requirements of practical applications. Thus, developing methods to prolong the life of Li-O₂ batteries is paramount for bringing Li-O₂ batteries to application.

Traditional methods to extend the life of Li-O₂ batteries include cathode material engineering³⁻⁵, electrolyte design⁶⁻¹¹, anode optimization^{12,13}, and interphase tuning¹⁴⁻¹⁷. However, the performance of Li-O₂ batteries is still far from satisfactory. In recent years, many new conceptual works have been conducted to further boost the life of Li-O₂ batteries, like changing the failed battery with a new cathode and regenerating the degraded cathode by acid wash and high-temperature pulse annealing^{18,19}.

Although effective, these changing-and-regenerating strategies involve tedious battery disassembly and reassembly procedures, which need to be conducted by professionals. In application scenarios, detailed processes, like battery collecting, transferring, reassembling, and quality check must be done before usable batteries can be realized, greatly increasing the time and cost, which may not be as economical as assembling new batteries (Fig. 1a). Therefore, we suppose whether the cathode can be in-situ revived without battery disassembly, thus extending the life of Li-O₂ batteries while reducing the cost. Since the side products induced cathode degeneration mainly originates from the poor charge efficiency of Li-O₂ batteries, then the questions move to whether we can compensate for the low efficiency by extra charge capacity?

For Li-ion batteries (LIBs), overcharge should be avoided due to the consequent negative impacts, including Li deposition on the anode, electrolyte decomposition, cathode structure changes, and capacity fading^{20,21}. More seriously, overcharge could also lead to gas generation and heat accumulation in the closed system of LIBs^{21,22}. Consequently, swelling, rupture, thermal runaway, firing, and even explosion may happen, which pose serious threats to human and device safety. On the contrary, the semi-open nature of Li-O₂ batteries makes it possible to withstand the overcharge, since the gases generated from side reactions can be liberated, and the flowing gas can take heat away to prevent its accumulation. Therefore, the safety of Li-O₂ batteries can be ensured under abusive conditions, like nail penetration, crushing, and high-temperature tests^{23,24}. In addition, the semi-open system of Li-O₂ batteries also makes electrolyte addition easier than the closed system of LIBs or Li-metal batteries, thus we can supplement fresh electrolyte to avoid its degradation including capacity fading and battery failure²⁵. Hence, the unique structure of Li-O₂ battery enables it to endure overcharge in a secure manner and prevent the electrolyte from drying up.

Herein, with Li-O₂ battery as an object for detailed research, we demonstrate that overcharge metal-O₂ batteries can prolong the life significantly. The excess amount of Li anode used in the battery makes the culprit of the initial battery failure come from the cathode passivation, which is induced by continuous side products accumulation and poor charge efficiency. These accumulated side products can be removed through conducting a simple overcharge step, leaving the buried active sites and blocked electron transfer pathways recovered for further proceeding the electrochemical reactions, thus the cathode life of Li-O₂ batteries is greatly extended to 1316 cycles. When introducing CO₂ into the O₂ reaction gas to protect the Li anode, the lifespan can be further prolonged, reaching an ultrahigh value of 2714 cycles. Furthermore, overcharge can enable the Li-O₂ battery to be fully discharged at higher capacities for more than 20 cycles. We also checked the application of overcharge in Li-O₂ batteries with high-loading cathodes (5 mg cm⁻² Ru/CNT), the battery with high cathode loading ran for 900 cycles at 1 mA cm⁻² and 0.2 mAh cm⁻². Importantly, this overcharge method is also applicable to Na-O₂ and K-O₂ batteries. The great performance improvement enabled by overcharge redefines its functions in batteries by prolonging the life of metal-O₂ batteries in an easy, time-saving, and cost-effective way.

Results

The benefits of overcharge in Li-O₂ batteries. Figure 1b depicts the proposal of cathode regenerating by overcharge. A new Li-O₂ battery consists of fresh Li anode and carbon cathode. During battery cycling, the parasitic reactions and poor rechargeability will result in side product accumulating on the cathode. When the cathode is passivated to some extent, the discharge voltage will plummet to lower than 2.0 V, a sign of battery failure^{4,26}. The failed battery is considered useless in most previous investigations. However, at this stage, the anode is not fully utilized because of its excess amount. Disposing the failed battery will lead to safety problems owing to the active nature of lithium and result in resource waste. Therefore, the failed batteries should be recycled to meet the demand for a sustainable and green society. Nevertheless, the traditional procedures for battery recycling are complicated, time-consuming, and costly (Fig. 1a), which will increase the price of the renewed battery. In contrast, the battery regenerated by a simple overcharge process can prolong the battery life and maintain a low cost simultaneously. As can be seen from Fig. 1B, after overcharge, the passivation layer on the cathode can be removed, thus providing free space for the deposition of following discharge product and battery cycling. This overcharge strategy can be used many times until the exhaustion of active Li. This brings another benefit. If there remain residue Li in the battery, risks of firing and explosion exist during reservation and transportation because of its active nature. However, LiOH is much safer and easily recycled without considering the Li processing (Fig. 1c). At this time, the battery components realize system-level efficient use, and the failed battery is safer and easy to be collected and recycled.

Cathode passivation and overcharge to remove passivation. To confirm the assumptions above, we first verified that the cathode passivation resulted in the initial battery failure, rather than the Li anode. As shown in Fig. 2a, the newly assembled Li-O₂ battery can run for 100 cycles at a current density of 44.2 $\mu\text{A cm}^{-2}$ and a fixed capacity of 44.2 $\mu\text{Ah cm}^{-2}$. After the battery failed (discharge voltage dropped to 2.0 V), the cathode and anode were decoupled to pair with a fresh anode and cathode, respectively, to assemble new batteries to check their viability. From Fig. 2b we can see that the battery with the new cathode can run normally without discharge voltage drop for 10 cycles, indicating good cooperation of the new cathode and the remnant of active Li in the old anode. However, even at the 1st cycle, the battery with the used cathode and fresh Li plate can hardly work with a steep discharge voltage drop to 1.0 V (Fig. 2c). As expected, overcharging the battery at 17.7 $\mu\text{A cm}^{-2}$ for 10 h enables it to deliver a higher discharge voltage in the subsequent cycles even though the voltage decrease gradually. This performance recovery should be attributed to the overcharge induced cathode side product decomposition. Furthermore, the status of the cathode and anode in the initially failed battery was checked. The X-ray diffraction (XRD) patterns of the Li anode show strong peaks of LiOH, but Li peaks still exist (Fig. 2d). The relatively weak signals for Li are due to the upper thick LiOH shielding layer ($\sim 131 \mu\text{m}$, Supplementary Fig. 1). This means that only 30% active Li is consumed after first battery failure and the residue Li could be a safety threat if not being handled properly during battery recycling procedures. For the cathode, the pristine CNTs with clean surface are totally covered by thick side products (Supplementary Fig. 2), and these side products are in amorphous states since there are no characteristic peaks from Li₂O₂, Li₂CO₃, or other species (Fig. 2e).

These results unambiguously identify that the reason for the initial battery failure is from the cathode passivation, supporting the assumption of reviving the failed battery by following the procedures in Fig. 1b.

So the question is what causes the side product accumulation on the cathode. To check the reason, the cathode morphologies after discharge and charge for 0.1, 0.2, 0.4, and 0.8 mAh (Supplementary Fig. 3) at 0.05 mA were examined. When the fixed capacity is small (0.1 or 0.2 mAh), the cathode structure can be recovered and most of the products can be removed after charge (Supplementary Fig. 3a,b). Even though the undecomposed product is negligible in these small capacities, it can be a tough problem in high-capacity cycling. When the capacity is increased to 0.4 mAh, a passivation layer can be observed on the cathode after charge (Supplementary Fig. 3c). Further enlarging the capacity to 0.8 mAh, except the passivated film, particle agglomeration emerges (Supplementary Fig. 3d), indicating that the amount of side product increases with the enlargement of discharge capacity. The poor charge efficiency of Li-O₂ batteries can also be reflected on the discharge and charge profiles. In Supplementary Fig. 4a, when the charge capacity reached the discharge value (0.39 mAh), the voltage just experiences a slight increase and follows a quick rise at 0.45 mAh due to the decomposition of the electrolyte. However, for the battery with a much higher discharge capacity of 2.74 mAh, there is almost no voltage change when being charged to the same capacity (Supplementary Fig. 4b). Even charged to 3.22 mAh, only a weak voltage increase emerges, implying that the reactions between 2.74–3.22 mAh are identical to those before 2.74 mAh. This means that, if cycling the battery at the capacity-limited mode and high discharge depth, more undecomposed products will accumulate on the cathode, and the poor charge efficiency will be amplified. As cycling continues, the constant accumulation of the undecomposed product will completely passivate the cathode and cause the death of the battery.

The morphology and composition evolution of the undecomposed product after different cycles were then characterized. After the 10th discharge, the discharge products cover the CNT cathode (Fig. 3a) and their composition has been confirmed by the Fourier transform infrared (FTIR) spectra with the existence of Li₂O₂ (500–600 cm⁻¹) and Li₂CO₃ (880 and 1400–1520 cm⁻¹) (Supplementary Fig. 5). Although most of the discharge products decompose and a clear CNT structure is observed during the following charge process (Fig. 3b), there still remain some undecomposed Li₂O₂ and Li₂CO₃ connecting the CNTs. After 50 cycles, more products deposited on the discharged cathode (Fig. 3c), and they almost exhibit no decomposition after the charge process (Fig. 3d), accompanied with strong peaks from Li₂CO₃, Li₂O₂, and HCOOLi (Supplementary Fig. 5), revealing the continuous accumulation of these products on the cathode. After confirming the composition of the undecomposed products, we subsequently checked the reactions happening during the overcharge process by monitoring the pressure of the battery to quantify the change of gas. Supplementary Fig. 6a gives the cycling performance of a Li-O₂ battery at 0.1 mA with a fixed capacity of 0.4 mAh. At the 17th cycle, the discharge voltage drops to 2.0 V and then the battery has been charged for 12 h at 0.1 mA. The pressure change of the battery at this cycle is shown in Supplementary Fig. 6b. The discharge process shows a 2.09 e/O₂ reaction, suggesting Li₂O₂ is the main discharge product. However, during overcharge, the coefficient is much higher than 2, reaching 4.01 e/O₂,

indicating severe side reactions happen, including the decomposition of previous accumulated products and the high voltage (> 4.5 V) induced electrolyte degradation. Besides, the coefficient is a constant value during the whole overcharge process, suggesting similar electrochemical reactions continuously happen. After overcharge, the battery can work normally with a discharge plateau around 2.6 V (Supplementary Fig. 6b). Since we have demonstrated that the initial battery failure is caused by the cathode passivation, the revival of the battery can be attributed to the removal of the accumulated products on the cathode by overcharge, which is visualized in Supplementary Fig. 7. After 15 cycles, the cathode is covered by a passivation layer (Supplementary Fig. 7a). It is clear that overcharging the battery for 4 hours can remove most of the previously deposited products, leaving only minor aggregates (Supplementary Fig. 7b). When the overcharge time is extended to 8 h, the deposited products can be completely removed (Supplementary Fig. 7c), recovering the cathode to the fresh state with exposed active sites and ample free space. Therefore, the impedance of battery decreases with longer overcharge time (Supplementary Fig. 8).

The above discussions have verified that the gradual increase of the passivation product with prolonging the cycling number is due to the negative impact of the poor charge efficiency of Li-O₂ batteries. To quantify the amount of the accumulated products after different cycles, acid-base titration measurement was conducted. As shown in Fig. 3e, the Li-containing products increase as cycling goes on even though the increasing trend is not linear. This has confirmed the residue products accumulation on cathodes during cycling. The EIS results in Fig. 3f also show a higher impedance at the 10th cycle than the 1st cycle. When the battery failed at the 85th cycle, the impedance further increases and is much higher than the initial value owing to the significant amount of undecomposed products accumulated on the cathode. However, after overcharging for 10 hours, the impedance recovers to a normal value and the battery can be further cycled for another 14 cycles. It should be noted that the strategy of reviving the battery by overcharging can be done many times until the active Li is used up.

Overcharge realizing long-life Li-O₂ batteries. Now that we have demonstrated that overcharge can indeed remove undecomposed products on the cathode and revive the battery for further cycling, the long cycling performance of Li-O₂ battery with overcharge deserves testing to fully take its advantage. As shown in Fig. 4a,b, the Li-O₂ battery fails after 180 cycles, and a 4-hour overcharge enables the battery to work normally for extra 10 cycles before the next voltage dropping to 2 V at 387 h (Fig. 4b). Every time the battery fails, overcharge is conducted and thus repeating many times. It is necessary to mention that, for Li-O₂ battery, the electrolyte is constantly consumed during cycling because of side reactions and volatilization. Adding electrolyte to the battery can no doubt help extend the battery life as well, and this is possible due to the semi-open structure of Li-O₂ battery and can be easily achieved without the requirement of battery disassembly like LIBs. Therefore, when overcharge cannot revive the battery, about 150 μ L electrolyte was added (Fig. 4c). After electrolyte wetting, the battery can run again and the discharge voltage plateau recovers. In the following cycles, 4-hour-overcharge was adopted when the battery failed. After 624 cycles (1320 h), the anode was exhausted (Fig. 4f) and a new anode was coupled with the original cathode to assemble a battery. Surprisingly, this battery could keep running with

a stable discharge plateau (Fig. 4d). The overcharge, electrolyte addition, together with refreshment of the Li anode finally enable the Li-O₂ battery to deliver a long life of 1316 cycles (Fig. 4e). Seeing the cathode can be continuously regenerated by overcharge and the easy addition of electrolyte to the battery, the life of the Li-O₂ battery is limited by the durability of the Li anode (Fig. 4a). Hence, adopting Li protection strategies can further improve the battery performance. In our previous work, we verified that CO₂ could stabilize the Li-O₂ batteries by forming a protective Li₂CO₃ layer on the Li anode and capturing superoxide radical (O₂^{-•})²⁷. Furthermore, a Li-O₂/CO₂ battery was constructed to take full advantage of the cathode and anode and further extend the battery life (Supplementary Fig. 9a). The Li-O₂/CO₂ battery first fails after 92 cycles, followed by a 4-hour overcharge, and then it works normally again (Supplementary Fig. 9b). As expected, the integration of overcharge and electrolyte addition eventually makes the Li-O₂/CO₂ battery realize a record-high lifetime, reaching 2714 cycles (Supplementary Fig. 9 and Fig. 5a, ~ 270 days). The stabilization effect on Li anode can be proved by the clean surface after 626 cycles (Supplementary Fig. 10a). However, the ultimate failure of the Li-O₂/CO₂ battery is resulted from the Li anode pulverization and exhaustion because of this ultra-long cycling (Supplementary Fig. 10b), thus we believe the battery could live longer if a better anode protection strategy can be developed in the future.

The cumulative capacities of the Li-O₂ battery and Li-O₂/CO₂ battery are 9.5 and 4.6 mAh respectively before the first failure. With overcharge, the cumulative capacities are enlarged to 65.85 mAh for Li-O₂ battery and 135.7 mAh for Li-O₂/CO₂ battery (Fig. 5b). This great improvement should be ascribed to the effective revival of the degraded cathode by overcharge. Furthermore, we conducted battery cycling tests at full discharge state (discharge to 2.0 V) and checked the capacity retention by overcharging the battery with additional 1/10, 1/5, and 1/3 discharge capacity (Supplementary Fig. 11). The battery without overcharge displays the poorest capacity retention, only ~ 20% of the initial capacity can be delivered at the 6th cycle (Fig. 5c). For the overcharged batteries, the two with 1/10 and 1/5 overcharge have comparable capacity retention rate, about 40% after 20 cycles, while only 14.56% and 6.35% remain for the batteries without overcharge and with 1/3 overcharge. The total capacities of the four batteries delivered in the first 20 cycles are 4.54, 11.60, 11.19, 6.99 times their first discharge capacities (Supplementary Fig. 11e), respectively, meaning that the degree of overcharge is not the higher, the better, but should be rationally controlled.

We further checked whether overcharge could prolong the life of Li-O₂ batteries with a redox mediator. A Li-O₂ battery with 50 mM Lil in the electrolyte was tested at 200 mA/g with a capacity of 2000 mAh/g. As shown in Supplementary Fig. 12, just after 15 cycles, the battery fails. After overcharge, the battery can run another 5 cycles. Then overcharging again, the battery runs for more than 56 cycles. The final life of the battery is 88 cycles, ~ 5 times longer than the initial 15 cycles.

Overcharge in Li-O₂ batteries with high mass loading. We acknowledge that the development of Li-air batteries is still far from extensive application because of many unsolved problems, including the small active material loading on cathode. In the future, mass loading should be increased from submilligram to milligram level to boost capacity and cycling life. To prove the potential of this strategy in real-world

application, Li-O₂ batteries with 5 mg Ru/CNT on carbon paper (1 cm²) as cathodes were tested. After battery failure, the surface of Ru/CNT was covered by residue products (Fig. 6a). After overcharge, the residue was decomposed, leaving uncovered CNT structures clearly, which proves that the overcharge can remove the excessive products even in cathodes with such a high mass loading. Then the battery cycling performance was checked at different conditions. Figure 6c exhibits the performance at 0.5 mA cm⁻² with fixed capacity of 0.2 mAh cm⁻². After 47 cycles, the discharge voltage dropped to below 2.0 V, indicating the first failure. However, the battery revived by charging to 0.4 mAh cm⁻², doubling the normal charge capacity. By doing so, the battery can be revived more than 60 times, and the battery life was extended to 907 cycles, far exceeding the initial 47 cycles. We further lifting the current density to 1 mA cm⁻² with the same capacity. Similar to the battery in Fig. 6c, this battery failed after a short time (24 cycles). Then the battery was overcharged repeatedly to prolong its life. Surprisingly, 900 cycles were achieved at such a high current density (Fig. 6d). In addition, batteries with higher capacities (0.5 mAh cm⁻² and 1 mAh cm⁻²) are checked in Supplementary Fig. 13. The batteries cycled at 0.5 mA cm⁻² and 0.5 mAh cm⁻², 0.2 mA cm⁻² and 1 mAh cm⁻² achieved 325 cycles and 91 cycles respectively, far exceeding the original cycles. Given that high loading is less used in Li-O₂ batteries, a list has been made to compare the battery performances (Table S1).

We note that no extra electrolytes were added during the long cycling and even the cathode loading increased to 5 mg, the amount of electrolyte added during battery assembly was kept at 130 μL despite the thicker cathode (419 μm). One abnormal phenomenon has attracted our attention, at the later stage of the cycling, each overcharge can enable more cycles (25000–45000 min in Fig. 6c and 13500–22000 min in Fig. 6d). In addition to the solvent evaporation, the decompositions of electrolyte and Li₂O₂ are competing reactions and proceed simultaneously during charge. When the batteries were disassembled, the electrolyte was totally drained. We anticipate that electrolyte has dried up before the final failure and the decomposed electrolyte has transformed to solid-state electrolyte (SSE) after decomposition to sustain the battery life. The formed SSE was more stable than the liquid, thus the decomposition of Li₂O₂ prevailed. Then the accumulation of product was alleviated and the battery life extended naturally

General applicability of overcharge in metal-O₂ batteries. The above batteries were all based on CNTs cathodes. To check whether overcharge is also effective in ordinary carbons to improve the performance, Super P cathode was used as an example to configure a Li-O₂ battery. The battery only delivers a life of 31 cycles in traditional evaluation criterion and the life can be extended to 98 cycles with the help of two times of overcharge (Supplementary Fig. 14), proving that overcharge is a general method to regenerate the carbon-based cathodes. We anticipate carbon-free cathodes can further improve the performance due to the decrease of side reactions.

Moreover, overcharge is not only effective in Li-O₂ batteries but also applicable in Na- and K-O₂ batteries. For the Na-O₂ battery, the first failure happens after 73 cycles, and overcharging twice enables the battery to work for 60 more cycles (Supplementary Fig. 15a). The thick solid electrolyte interphase (SEI) formed on the Na anode may be the reason of the large overpotential (Supplementary Fig. 15b). The K-O₂ battery

is very unstable with discharge voltage dropping to 2.0 V only after 8 cycles. Since there are limited undecomposed products deposited on the cathode with this short life, the battery failure is presumably caused by the anode side. After overcharge, the battery revives with much longer life and higher overpotential, probably due to the overcharge induced electrolyte decomposition that enables the formation of a stable SEI on the K anode. In the following battery failure, the function of overcharge is to decompose the accumulated products on cathode. Finally, the battery runs for 123 cycles, much longer than the initial 9 cycles without overcharge (Supplementary Fig. 15c). After disassembling the battery, we find that there is even thick SEI on the backside of the K anode (Supplementary Fig. 15d), resulting in a higher overpotential.

Discussion

In summary, this work has identified that cathode passivation is the reason for the initial Li-O₂ battery failure and discussed the feasibility of extending the battery lifespan by overcharge. The discharge products and side products cannot be totally decomposed during the following fixed-capacity charge process due to the poor charge efficiency of the Li-O₂ battery, thus a passivated layer forms on the cathode. As cycling goes on, this passivated layer continually accumulates and finally blocks the reaction sites and electron transfer pathways on the cathode, leading to the failure of the battery. After overcharge, the fatal passivated layer on the cathode can be removed to re-expose the active sites and rebuild the electron transfer pathways, reviving the failed Li-O₂ battery and finally extending the battery life from 180 to 1316 cycles.

Besides, the battery life can be further prolonged by introducing CO₂ into the O₂ reaction gas to protect the Li anode, realizing system-level efficient use of each battery component thus a super-long life of 2714 cycles (more than 6300 h) without changing the anode. We expect that if a better anode protection strategy is applied, a longer-life battery could be achieved, even though it is very difficult. To demonstrate its potential in application, high-loading cathodes (5 mg/cm² Ru/CNT) were applied in Li-O₂ batteries at high current densities. Finally, ~ 900 cycles were achieved at 0.5 mA cm⁻² and 1 mA cm⁻² with a fixed capacity of 0.2 mAh cm⁻². This overcharge induced battery revival strategy is also applicable in Na- and K-O₂ batteries, which indicates that overcharge may be useful in other conversion-based batteries. Traditional methods including changing the spent cathode with a new one involve tedious battery disassembly and re-assembly, enabling the battery recycling and regeneration to experience complex processes. Our results have shown an easier and safer metal-O₂ battery recycling strategy. Moreover, overcharge has long been conceived to be destructive for battery performance, this work has reshaped this impression and may inspire more considerations on the concept differences between Li-ion batteries and new emerging battery technologies.

Methods

Materials. Lithium trifluoromethanesulfonate (LiCF_3SO_3 , 98%), Sodium trifluoromethanesulfonate (NaCF_3SO_3 , 98%), Potassium trifluoromethanesulfonate (KCF_3SO_3 , 98%), Tetraethylene glycol dimethyl ether (TEGDME, 99%), and Lithium iodide (LiI) were purchased from Aladdin. Before usage, the salts were dried in vacuum oven overnight at 130 °C. 1 M $\text{LiCF}_3\text{SO}_3/\text{TEGDME}$, $\text{NaCF}_3\text{SO}_3/\text{TEGDME}$, $\text{KCF}_3\text{SO}_3/\text{TEGDME}$ were used as electrolytes in Li-, Na-, and K- O_2 batteries, respectively. Super-dry acetonitrile and 1,3-Dioxolane (DOL, 99.8%, superdry, stabilized with BHT, water \leq 30 ppm) were bought from J&K Scientific. Multiwall carbon nanotubes (CNT) were purchased from Beijing DeKe Daojin Science and Technology Co., Ltd. Before using, TEGDME was dried with molecular sieves for more than 1 month. The water content of all electrolytes was determined to be less than 30 ppm by 831 KF Coulometer (Metrohm, Switzerland). The lithium plates (thickness, 400 μm , diameter, 14 mm) was bought from China Energy Lithium Co., LTD, Tianjin, China. High purity gas (O_2 , CO_2 and Ar) were supplied by Changchun Juyang Gas CLT, Changchun, China.

Cathode fabrication. Carbon nanotubes and PVDF were mixed at a mass ratio of 9:1 in NMP (N-methyl-2-pyrrolidone) to form a homogeneous slurry through grounding in a mortar. The slurry was then sprayed on a carbon paper followed by drying in a vacuum oven overnight. After this, the dried carbon paper was punched into round pieces (12 mm in diameter) to get cathodes. Several batches of cathodes were prepared and the mass loading range was 0.1–0.3 mg per cathode. The specific capacity was calculated based on the mass of active materials. For the Li- O_2 batteries with a high mass loading (5mg cm^{-2}) on cathode (Ru/CNT), the cathode was used as received. The total weight of the cathode material and carbon paper is \sim 10 mg. The total mass of the assembled battery is 0.192 g.

Battery assembly. The batteries were assembled based on ECC-Air models (EL-cell GmbH, Germany). The lithium plate (equivalent to 158 mAh) was put at the bottom, followed by the stacking the glass fiber separator (thickness, 300, diameter, 18 mm), and the prepared cathode (thickness, 200 μm). Therefore, the fabricated battery is about 900 μm in thickness. The amount of the electrolyte used in the battery is 130 μL . The battery was sealed in the model with a spring, when the battery thickness is 900 μm , the spring load is 15 N, thus the calculated pressure on battery is 1.33×10^5 Pa. This model makes flowing gas possible in Li- O_2 batteries. The flowing gas was 2 ml/min and the gas pressure in the battery is \sim 1 atm. After assembly, the batteries were transferred to a thermostatic tank (30°C) for resting at least 3 hours to ensure a pure gas environment before cycling.

Operando pressure test. The quantitative pressure test during battery cycling was based on an ECC-Press system (EL-Cell GmbH, Germany) connected with a VMP-300 electrochemical workstation (Biologic, France). Before test, the free volume of the battery system was determined by Boyle's Law. Then the system was purge by pure O_2 to remove the residue gas to ensure a pure O_2 environment. Then the system was sealed quickly to avoid gas permeation. This test must be tested in the thermostatic tank to minimize temperature fluctuation thus a smooth curve can be achieved.

Acid-base titration. The used battery was disassembled in air, and then the cathode was directly transferred into a bottle containing 5 ml deionized water. After shaking for 2 min to dissolve the side products, the solution was titrated by 0.01 M HCl with methyl orange as indicator. The titration point is determined by the color change from yellow to orange.

Characterizations. Before characterizations, the cathodes were washed with acetonitrile for three times to remove residue electrolyte, while the Li anodes were washed with DOL to remove residue glass fiber and electrolytes on its surface. Both the battery disassembling and electrode washing procedures were conducted in the glove box. After washing, the electrodes were dried in the air-lock chamber and then stored in the glove box. When testing the morphology of the electrodes, they were transferred to a sealed plastic bag to minimize air exposure. The SEM test was conducted on a field emission Hitachi S4800 scanning electron microscope and the X-ray diffraction characterization was performed on a MiniFlex 600 (Rigaku, Japan) X-ray diffractometer. FTIR measurement was carried out on a Nicolet 6700 spectrometer. Battery cycling tests were conducted on a LAND (CT2100A) multi-channel battery testing system. Electrochemical impedance spectra (EIS) were performed on the VMP-300 electrochemical workstation.

Data availability

The data are available within the paper and its Supplementary information file or from the corresponding author upon reasonable request. Source data are provided with this paper.

Declarations

Acknowledgements

The authors thank the supports from the National Key R&D Program of China (2017YFA0206700), National Natural Science Foundation of China (21725103), the Strategic Priority Research Program of the Chinese Academy of Sciences (XDA21010210), Jilin Province Science and Technology Development Plan Funding Project (20200201079JC), Changchun Science and Technology Development Plan Funding Project (19SS010), Jilin Province Capital Construction Funds Project (2020C026-1) & the K. C. Wong Education Foundation (GJTD-2018-09).

Author contributions

K.C. and X.-B.Z. conceived this research. K.C. carried out most of the experiments. D.-Y.Y and J.W. performed the FT-IR and Raman tests. D.-Y.Y conducted the operando gas monitoring during cycling. K.C., J. W. and G.H. discussed, analyzed the results. K.C, G.H. and X.-B.Z wrote and revised the manuscript.

Competing interests

A Chinese patent CN202010312976.8 has been filed. The authors declare no other competing interests.

Additional information

Supplementary information The online version contains supplementary material available at XX.

References

1. McCloskey, B. D. et al. Twin problems of interfacial carbonate formation in nonaqueous Li-O₂ batteries. *J. Phys. Chem. Lett.* **3**, 997–1001 (2012).
2. Mahne, N. et al. Singlet oxygen generation as a major cause for parasitic reactions during cycling of aprotic lithium-oxygen batteries. *Nat. Energy* **2**, 17036 (2017).
3. Xu, J. J., Wang, Z. L., Xu, D., Zhang, L. L. & Zhang, X. B. Tailoring deposition and morphology of discharge products towards high-rate and long-life lithium-oxygen batteries. *Nat. Commun.* **4**, 2438 (2013).
4. Xu, J.J. et al. Synthesis of perovskite-based porous La_{0.75}Sr_{0.25}MnO₃ nanotubes as a highly efficient electrocatalyst for rechargeable lithium-oxygen batteries. *Angew. Chem. Int. Ed.* **52**, 3887–3890 (2013).
5. Ottakam Thotiyl, M. M. et al. A stable cathode for the aprotic Li-O₂ battery. *Nat. Mater.* **12**, 1050–1056 (2013).
6. Yu, Y. et al. A renaissance of N,N-dimethylacetamide-based electrolyte to promote the cycling stability of Li-O₂ batteries. *Energy Environ. Sci.* **13**, 3075–3081 (2020).
7. Yu, Y. & Zhang, X. B. In situ coupling of colloidal silica and Li salt anion toward stable Li anode for long-cycle-life Li-O₂ batteries. *Matter* **1**, 881–892 (2019).
8. Aetukuri, N. B. et al. Solvating additives drive solution-mediated electrochemistry and enhance toroid growth in non-aqueous Li-O₂ batteries. *Nat. Chem.* **7**, 50–56 (2015).
9. Jung, H. G., Hassoun, J., Park, J. B., Sun, Y. K. & Scrosati, B. An improved high-performance lithium-air battery. *Nat. Chem.* **4**, 579–585 (2012).
10. Chen, Y., Freunberger, S. A., Peng, Z., Fontaine, O. & Bruce, P. G. Charging a Li-O₂ battery using a redox mediator. *Nat. Chem.* **5**, 489–494 (2013).
11. Gao, X., Chen, Y., Johnson, L. & Bruce, P. G. Promoting solution phase discharge in Li-O₂ batteries containing weakly solvating electrolyte solutions. *Nat. Mater.* **15**, 882–888. (2016).
12. Ma, J. L. et al. Prevention of dendrite growth and volume expansion to give high-performance aprotic bimetallic Li-Na alloy-O₂ batteries. *Nat. Chem.* **11**, 64–70 (2019)
13. Lee, D. J., Lee, H., Kim, Y. J., Park, J. K. & Kim, H. T. Sustainable redox mediation for lithium-oxygen batteries by a composite protective layer on the lithium-metal anode. *Adv. Mater.* **28**, 857–863 (2016).
14. Asadi, M. et al. A lithium–oxygen battery with a long cycle life in an air-like atmosphere. *Nature* **555**, 502–506 (2018).

15. Xin, X., Ito, K., Dutta, A. & Kubo, Y. Dendrite-free epitaxial growth of lithium metal during charging in Li-O₂ batteries. *Angew. Chem. Int. Ed.* **57**, 13206–13210 (2018).
16. Zhang, X. P., Sun, Y. Y., Sun, Z., Yang, C. S. & Zhang, T. Anode interfacial layer formation via reductive ethyl detaching of organic iodide in lithium-oxygen batteries. *Nat. Commun.* **10**, 3543 (2019).
17. Choudhury, S. et al. Designer interphases for the lithium-oxygen electrochemical cell. *Sci. Adv.* **3**, e1602809 (2017).
18. Liu, Q. C., Xu, J. J., Xu, D. & Zhang, X. B. Flexible lithium-oxygen battery based on a recoverable cathode. *Nat. Commun.* **6**, 7892 (2015).
19. Dong, Q. et al. A General Method for Regenerating Catalytic Electrodes. *Joule* **4**, 2374–2386 (2020).
20. Ren, D., Feng, X., Lu, L., He, X. & Ouyang, M. Overcharge behaviors and failure mechanism of lithium-ion batteries under different test conditions. *Appl. Energy* **250**, 323–332 (2019).
21. Pushnitsa, K. A., Kim, A. E., Popovich, A. A., Wang, Q. & Novikov, P. A. Structural transformation of LiNi_{0.8}Co_{0.1}Mn_{0.1}O₂ cathode material during cycling with overcharge investigated by in situ X-ray diffraction. *J. Electron. Mater.* **48**, 6694–6699 (2019).
22. Wu, L. et al. Structural origin of overcharge-induced thermal instability of Ni-containing layered-cathodes for high-energy-density lithium batteries. *Chem. Mater.* **23**, 3953–3960 (2011).
23. Zhao, S. et al. Failure analysis of pouch-type Li–O₂ batteries with superior energy density. *J. Energy Chem.* **45**, 74–82 (2020).
24. Liu, T. et al. Protecting the lithium metal anode for a safe flexible lithium-air battery in ambient air. *Angew. Chem. Int. Ed.* **58**, 18240–18245 (2019)
25. Louli, A. J. et al. Diagnosing and correcting anode-free cell failure via electrolyte and morphological analysis. *Nat. Energy* **5**, 693–702 (2020).
26. Xu, J. J., Wang, Z. L., Xu, D., Meng, F. Z. & Zhang, X. B. 3D ordered macroporous LaFeO₃ as efficient electrocatalyst for Li–O₂ batteries with enhanced rate capability and cyclic performance. *Energy Environ. Sci.* **7**, 2213–2219 (2014).
27. Chen, K. et al. The stabilization effect of CO₂ in lithium-oxygen/CO₂ batteries. *Angew. Chem. Int. Ed.* **59**, 16661–16667 (2020).

Figures

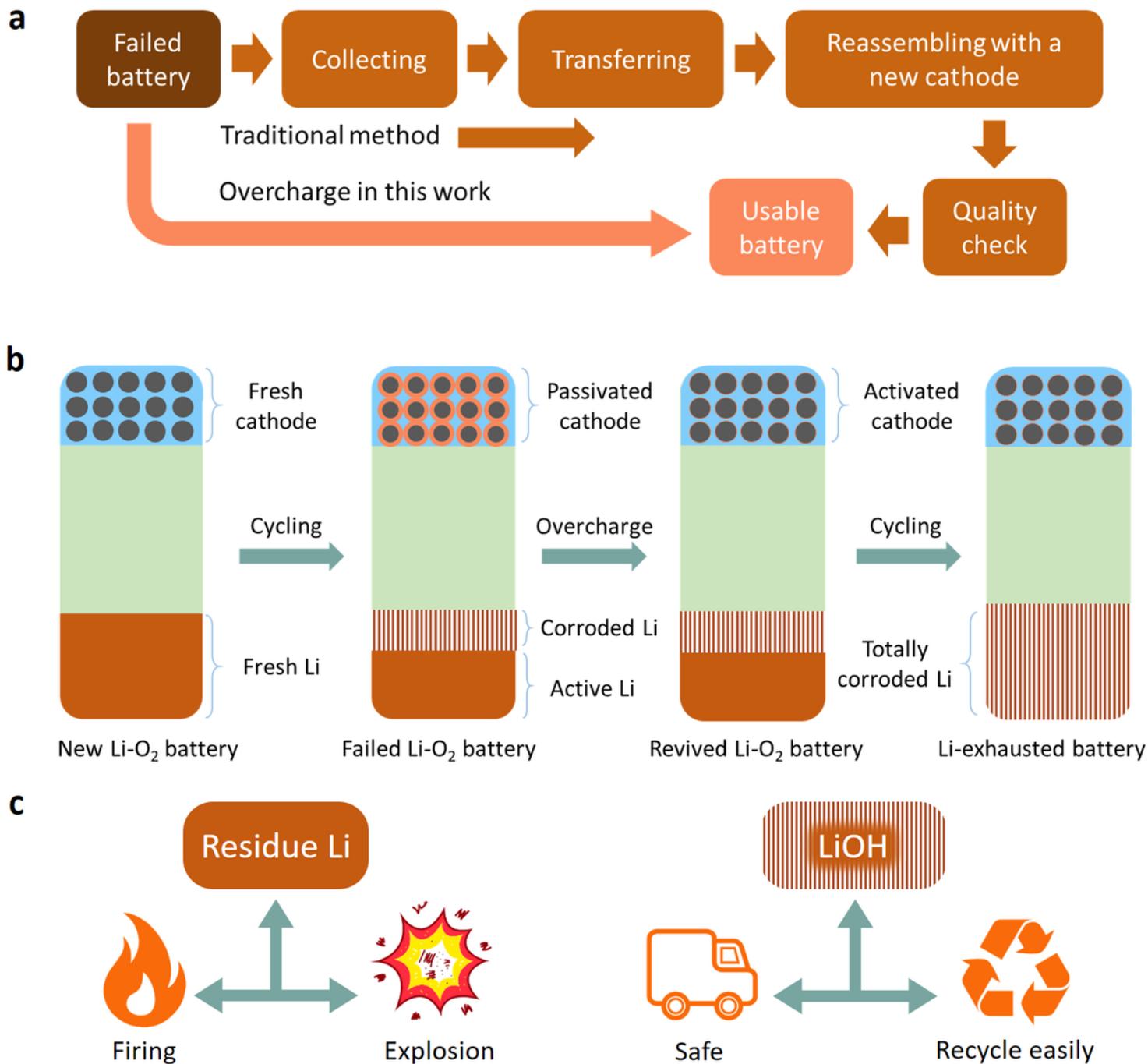


Figure 1

Comparison of traditional regenerating method and overcharge method for Li-O₂ batteries. a Two battery regenerating procedures. b Schematic illustration of overcharge method. c The comparison of properties of residue Li and LiOH in failed Li-O₂ batteries.

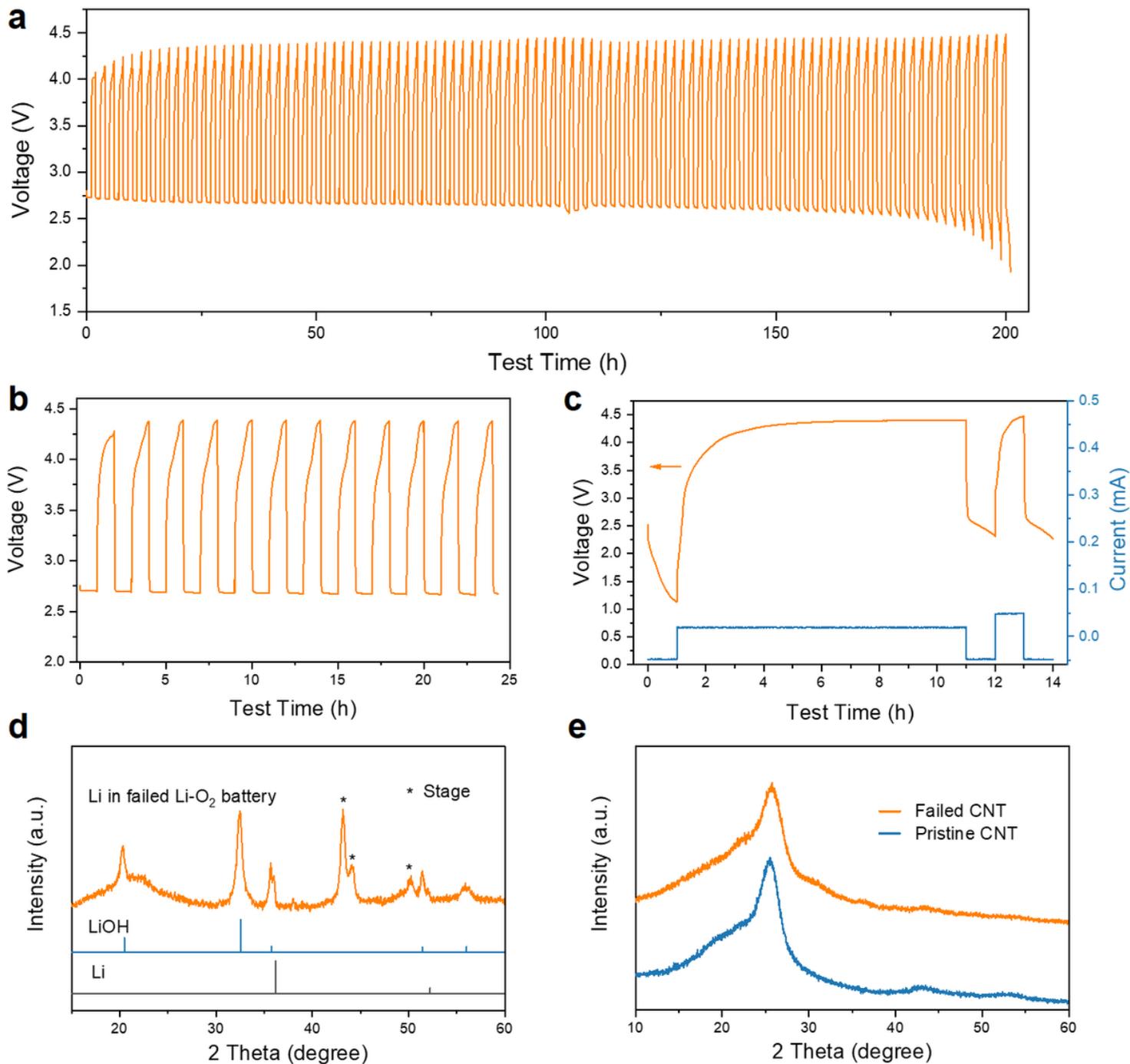


Figure 2

Identification of the failure reason for the Li-O₂ battery. a Cycling performance of a Li-O₂ battery at 44.2 $\mu\text{A cm}^{-2}$. b The new assembled battery with the used anode and a new cathode. c The new assembled battery with the used cathode and a new anode. d XRD pattern of the anode from the failed battery in (A). e XRD patterns of the pristine and failed cathode from the battery in a.

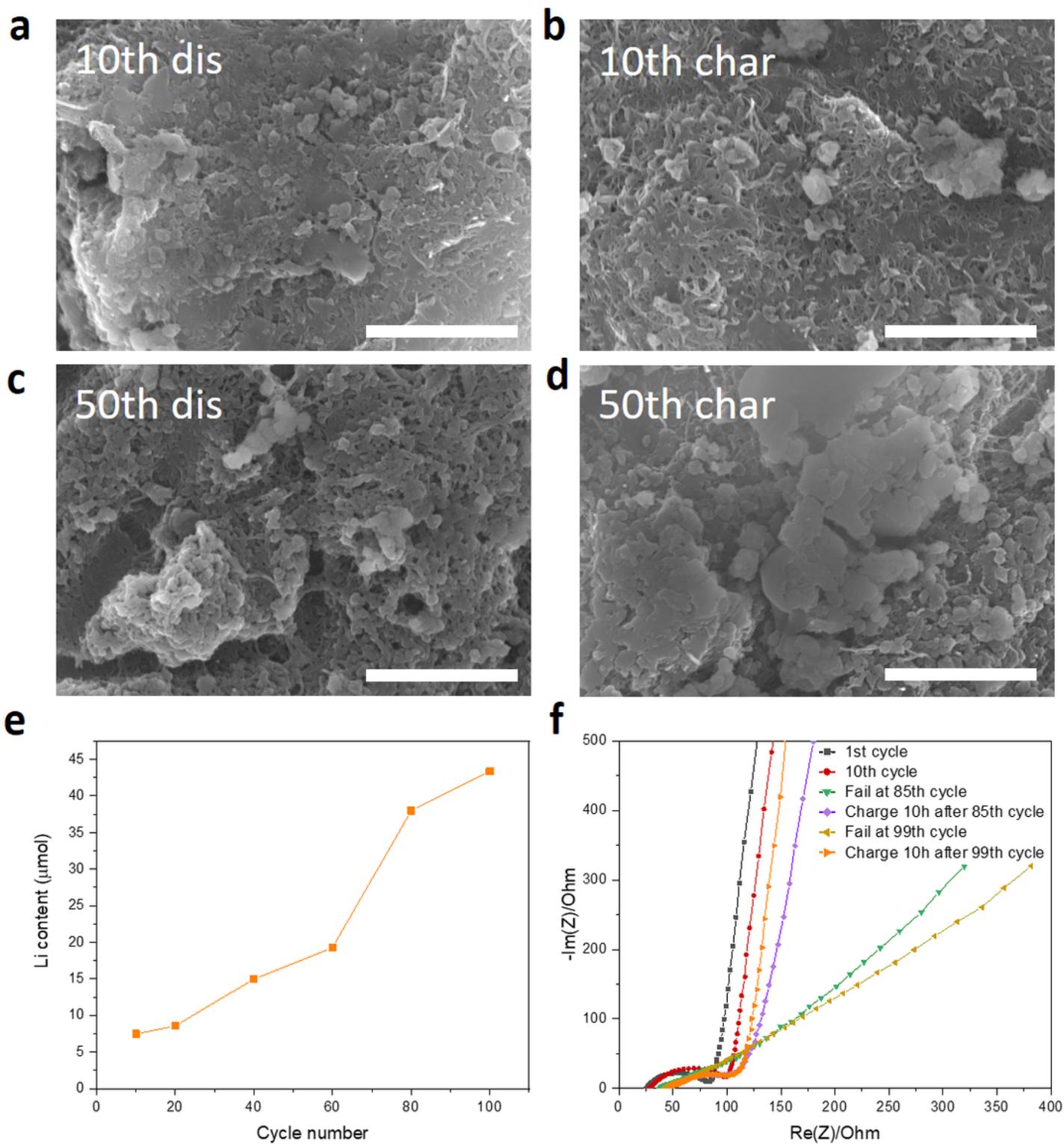


Figure 3

Accumulation of discharge products on cathodes. a-d Morphologies of cathodes after a 10th discharge, b 10th charge, c 50th discharge & d 50th charge. Scale bar, 2 μm . e Quantification of the products accumulated on cycled cathodes using acid-base titration method. f Electrochemical impedance spectra (EIS) of Li-O₂ battery at different stages.

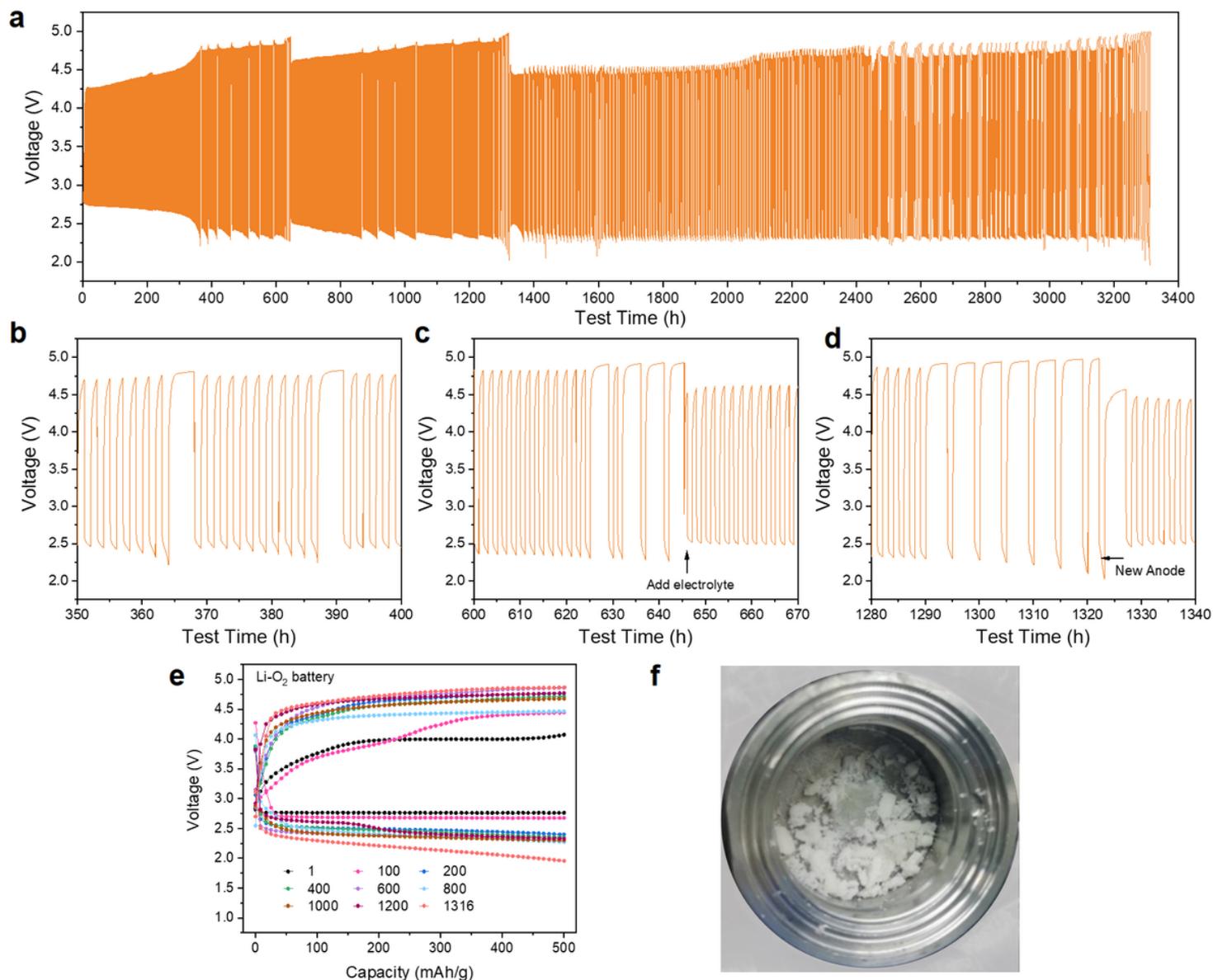


Figure 4

The effect of overcharge on the Li-O₂ battery. a Cycling performance of a Li-O₂ battery revived with overcharge (1316 cycles). b-d The enlargements of the profile in a. e Selected cycles from a. f A digital image of exhaustive Li anode after cycling. The current density is 500 mA/g and the capacity is 500 mAh/g.

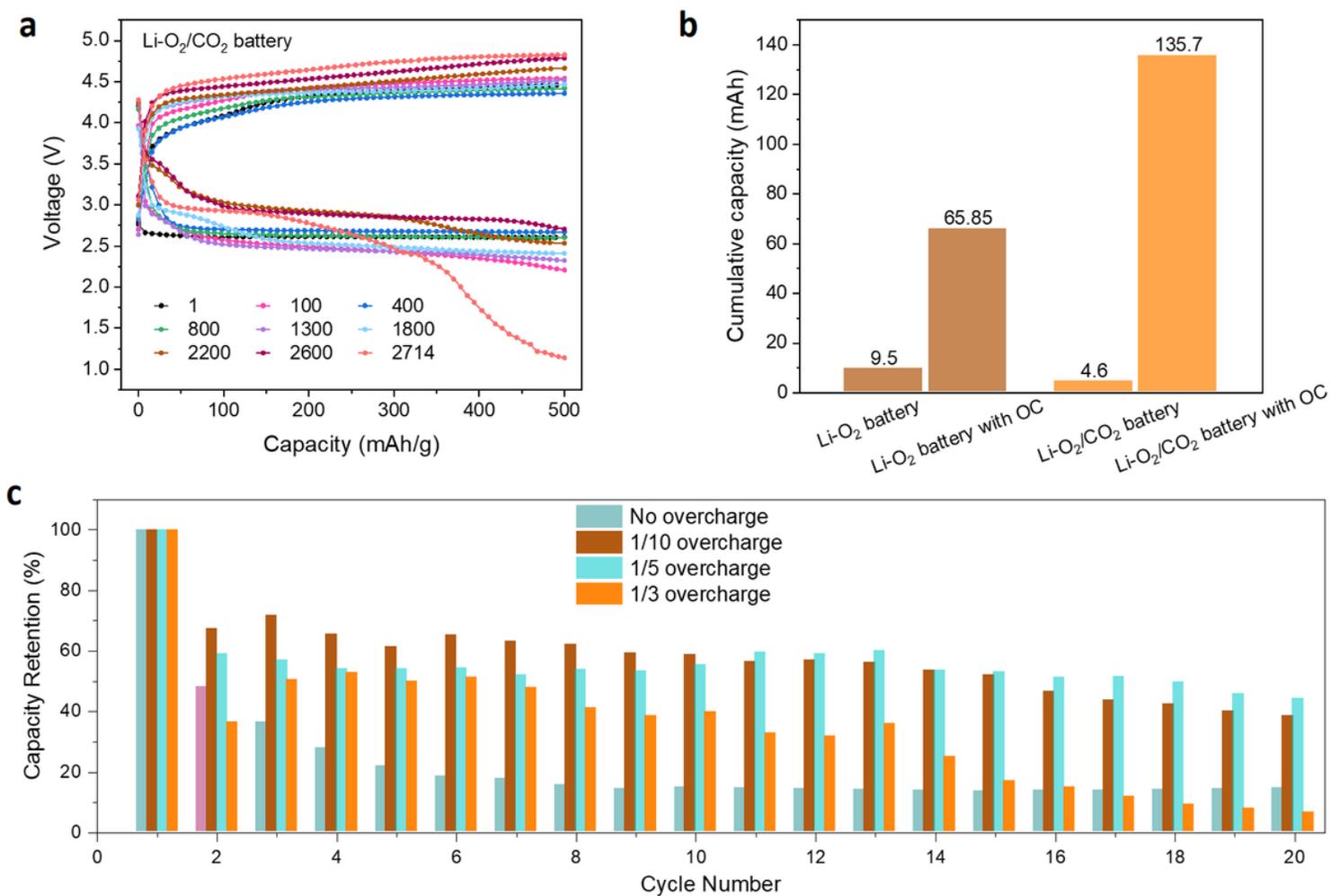


Figure 5

Battery performance characterization. a Cycling performance of Li-O₂/CO₂ battery at 500 mA/g and 500 mAh/g, revived with overcharge after battery failure. b Cumulative capacities of Li-O₂ and Li-O₂/CO₂ batteries with and without overcharge. c Capacity retention of Li-O₂ batteries in the first 20 cycles with different overcharge ratios.

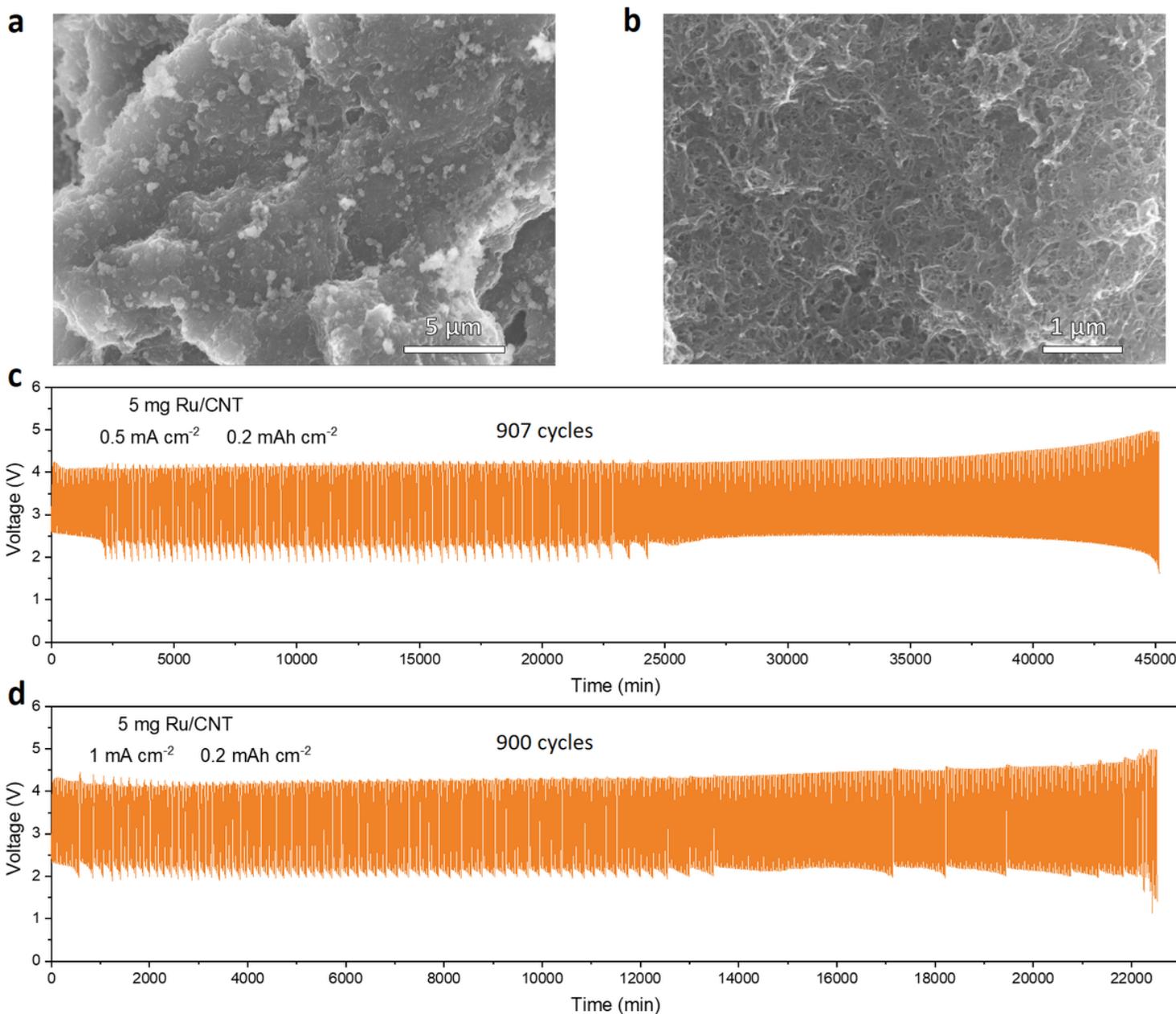


Figure 6

The Li-O₂ batteries with high mass loading (5 mg Ru/CNT as cathode). a Morphology of Ru/CNT cathode after battery failure. b Morphology of failed Ru/CNT cathode after overcharge. c Cycling performance of the Li-O₂ battery at 0.5 mA cm⁻² and 0.2 mAh cm⁻². d Cycling performance of the Li-O₂ battery at 1 mA cm⁻² and 0.2 mAh cm⁻². Overcharge in c,d means that the charge capacity doubles the discharge capacity.

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [SupportingInformation.docx](#)