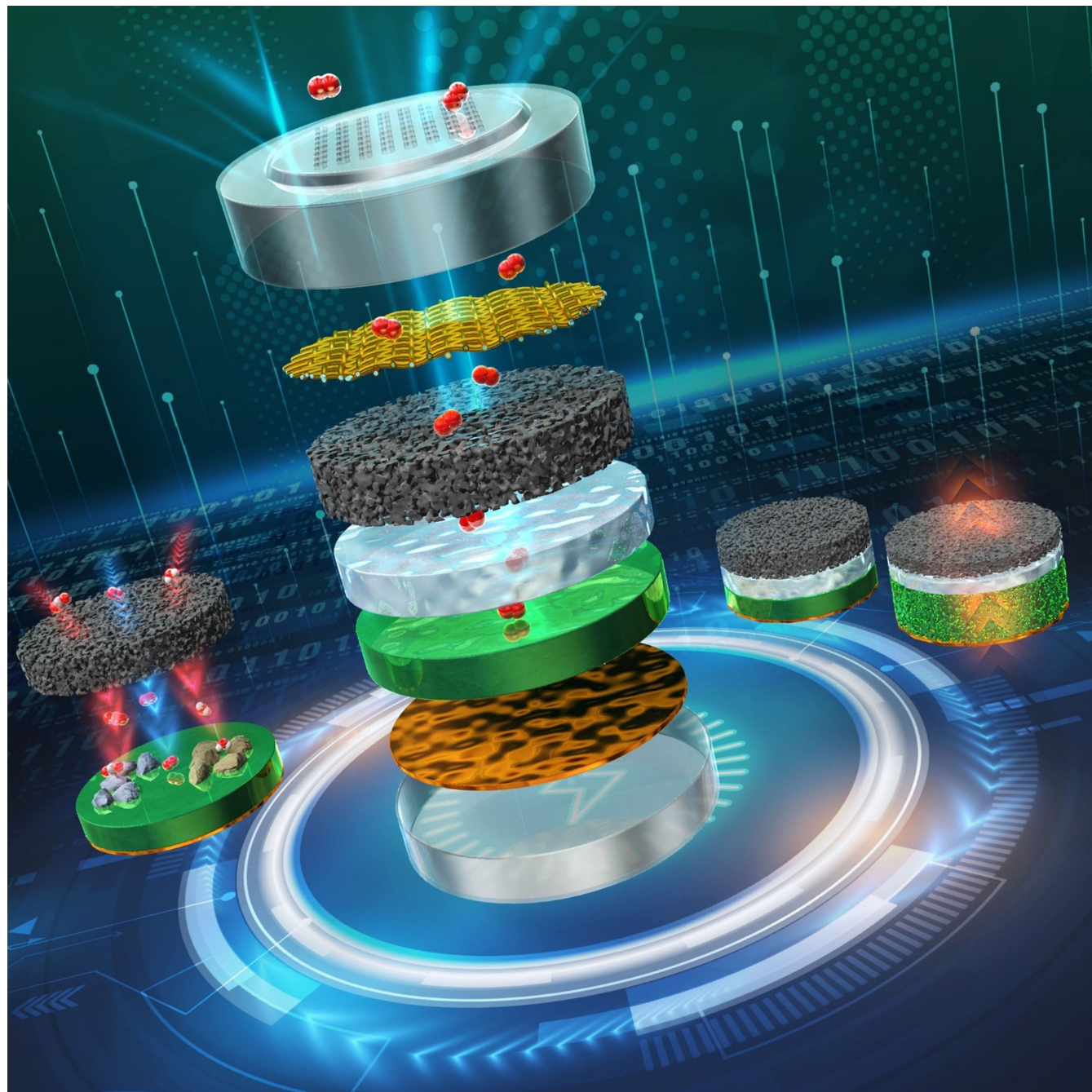


New Insights into Fundamental Processes and Physical Degradation Mechanisms in Rechargeable Lithium-Oxygen Batteries Providing Suitably High Energy Densities

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Lithium-oxygen batteries (LOBs) can exhibit high energy densities and so have attracted much attention as next-generation energy storage devices. Although 500 Wh/kg LOBs have recently been demonstrated, the performance of these batteries could still be greatly improved. This Concept article highlights the importance of exploring new technologies, such as gas-diffusion layers and lightweight protective membranes for lithium metal electrodes, as an approach to realizing LOBs having energy densities sufficient for practical applications. In

addition, the physical degradation phenomenon specific to LOBs designed with high energy density is also introduced, such as the volume change of the positive electrode and the movement of the electrolyte associated with the progress of repeated discharge/charge cycles. We believe that the topics presented in this article will promote new research directions in the future development of high energy density and long cycle life LOB.

1. Introduction

Lithium-oxygen rechargeable batteries (LOBs) are promising candidates for next-generation energy storage devices due to their potential to provide superior energy density values.^[1,2] In fact, recent studies have demonstrated the stable operation of 500 Wh/kg class LOBs that could exceed the energy densities of conventional lithium-ion batteries (LiBs).^[3] Even so, various technical issues still limit the practical commercialization of this technology, such as poor cycle lifespans (< 50 cycles), low power densities (< 50 Wh/kg) and slow charging rates (< 0.5 C). In addition, much higher energy densities above 700 Wh/kg at the cell level are highly demanded for various societal applications. To realize the improvement of these battery performances, the deep understanding of the reaction mechanism and the development of novel electrode/electrolyte materials are crucial. Recent advances in the main components of LOBs, such as electrolyte, carbon electrode and lithium metal electrode, are well summarized in recent reviews.^[4,5] At the same time, it is also necessary to develop the materials other than the above main materials, including gas diffusion layer (GDL), current collector and separator. Although these side components also have a large impact on the performance of LOBs, especially in practical high energy density conditions, the limited studies have been done for the development of these materials. In addition, with such material development, the deep understanding of the complicated reaction in LOBs is also crucial. Although previous studies mainly focused on the chemical/electrochemical reaction in oxygen positive electrode and lithium negative electrode, not only such chemical reaction but also physical degradation occurs in LOBs, in which the

reaction proceeds by formation and decomposition of solid-state products (Li_2O_2 and Li metal). Thus, there is concern about the large volume change of the electrode during repeated discharge/charge cycles. However, due to the difficulty of analyzing such a macroscopically complicated reaction in LOBs, the details remain unclear. Based on these considerations, in the present concept article, the present article summarizes the recent research progress on the unexplored fundamental technologies and physical degradation mechanism in LOBs with practically high energy density.

2. Design strategy for fabrication of LOBs possessing high cell-level energy density

2.1. Energy Density Simulations

Typical LOBs contain metallic lithium, which has a low redox potential of -3.04 V (vs. standard hydrogen electrode (SHE)) and a high theoretical capacity of 3860 mAh/g, and atmospheric O_2 as active materials. For example, assuming an operating voltage of 2.7 V, an energy density of 10422 Wh/kg can be obtained based on the mass of lithium metal (3860 mAh/g). This value corresponds to the energy density based on the active material (excluding the mass of oxygen in the atmosphere) before the discharge state. However, in practical conditions, the cell components such as electrolyte in the separator and porous carbon electrode are also taken into account to estimate the energy density based on the mass of the whole LOB cell.

To quantitatively understand the importance of the side component on the cell-level energy density of the LOBs, we estimate the energy density of the LOBs. The parameters used for this simulation are summarized in Table 1. The each components in LOBs were schematically illustrated in Figure 2a. For this energy density calculation, the capacity and mass loading of the carbon electrode are set to be 3000 mAh/g and 2 mg/cm², which are typical value as carbon electrode for high energy density LOBs.^[3] As a result, the areal capacity of the oxygen positive electrode is 6 mAh/cm². Polyolefin membrane with 20 μm thickness and lithium metal foil with 10 μm thickness were used as separator and negative electrode. The amount of electrolyte was estimated to completely fill the pore space in the carbon electrode and separator. In the following, we calculate the cell-level energy density of LOB in the fully

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discharged state (excluding the mass of oxygen) and average voltage of 2.7 V. Figure 1a exhibited the mass-based proportion of each component in standard LOB setup (Cell A). There can be seen that 10- μm -thick Cu foil with density of 8.8 mg/cm^2 and 200 μm -thick carbon fiber based GDL with density of 8.4 mg/cm^2 accounted for the greatest relative mass contribution. Here, the areal electric energy (Wh/cm^2) can be obtained by multiplying the average discharge voltage (V) and the areal capacity (mAh/cm^2). By dividing the areal electric energy by the total weight of the cell components, the cell level energy density of LOB can be obtained. In this energy density calculation, the weight of the sealing film, tab and lead are not contained. In case these weights are also included, the estimated energy density becomes approximately 10% lower value.^[6]

Next, let us consider the situation, in which the two heaviest components are replaced to lightweight materials (Cell B). This heavy current collector can be replaced with a Cu foil with a thickness of 2 μm . In addition, the GDL and current collector can be replaced with an integrated gas-diffusile current collector with mass loading of 1.3 mg/cm^2 . As results, the energy density of cell B reached to 563 Wh/kg (Figure 1b). Furthermore, replacing the lithium metal protective membrane of 10 mg/cm^2 with a membrane of 2 mg/cm^2 provided a value of 671 Wh/kg (Cell C). These results clearly demonstrate that decreasing the masses of various cell components, other than the carbon electrode and electrolyte, can greatly affect the cell-level energy density of an LOB. The following section provides an overview of recent research concerning the development of lightweight GDLs and protective membranes for lithium metal electrodes. Current collectors for negative electrodes having reduced masses have already been widely investigated based on research regarding LiBs, and the details of such work can be found in recent publications. Thus, a discussion of technological issues related to current collectors is outside the scope of this article.

2.2. Gas Diffusion Layer and Current Collector

The GDL is a specific material for LOBs, which function to facilitate efficient oxygen transport from outside the cell into the porous carbon electrode. Despite the importance of developing a lightweight and highly oxygen diffusible GDL material, the evaluation protocol for the GDL is not well



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established. From a practical point of view, multiple LOB cells need to be densely stacked, similar to conventional LiBs. In such stacked situations, proper cell configuration is required to ensure that oxygen can effectively pass through the entire positive electrode via the GDL.^[2] In particular, oxygen must be transported horizontally in the GDL. Then, oxygen must be further transported in the vertical direction to pass through the whole part of the positive electrode (Figure 2a). Therefore, the performance of the GDL should be evaluated in a suitable cell configuration in which the oxygen supply is allowed only through the horizontal direction of the GDL. However, in a coin-type cell or a swagelok-type cell, which are widely used for LOB study in the laboratory, the oxygen is supplied from the upper part of the positive electrode (Figure 2b). Therefore, the performance of the GDL cannot be properly evaluated in such a cell configuration.

We have recently proposed a single-layered cell with a 2 $\text{cm} \times 2$ cm sized electrode as a possible candidate for standard LOB cells, in which oxygen gas first needs to transport through the GDL in the vertical direction (Figure 1c). And then, oxygen gas further transports to inside of cell in the horizontal direction. Using such a setup, the concept of a gas-diffusible current collector was recently demonstrated, which combines the functions of oxygen mass transport and electron transfer with minimal mass loading.^[7] For the gas-diffusible current collector for high energy density LOB, the following three factors are crucial: (i) light weight, (ii) high electrical conductivity to function as an electron transport channel, and (iii) suitable structure for an oxygen transport channel. To verify this concept, nickel-coated polymer fiber meshes were fabricated, in which the PET fiber with diameter of 27 μm is fully covered with nickel with 0.5 μm thickness (Figure 2d–2g). The battery performance evaluation test revealed that LOB cells equipped with an ultralight gas-diffusible current collector exhibit equivalent discharge capacity with that of cells equipped with conventional heavy components at 0.4 mA/cm^2 , although, its weight is much smaller than that of conventional one (Figure 2h). These results suggesting that the use of nickel-coated polymer fiber meshes improve the energy density of LOB without diminishing their battery performance. As described in Section 2.1, the development of a lightweight GDL is critical to the realization of high energy density LOBs at the cell level. However, at present, the research attention for the development of GDL is quite limited. Intensive research attention is required for the development of advanced GDL materials to improve the performance of LOBs.

2.3. Separators Suppressing Chemical Cross-Over

For realizing long cycle life LOB, the protection of lithium metal electrode against atmospheric components and chemical cross overed compounds from positive electrode is crucial. In addition, many studies to date have utilized redox mediators to decrease the over-potential associated with charging. In such cases, it is helpful to apply a protective membrane to the lithium metal electrode to limit self-discharge due to the cross-

Table 1. Parameters used for energy density simulation of LOB.					
Cell		A	B	C	
Carbon membrane	Weight	2	2	2	mg/cm ²
	Thickness	100	100	100	μm
	Porosity	95	95	95	%
Separator	Weight	1.1	1.1	1.1	mg/cm ²
	Thickness	20	20	20	μm
	Porosity	45	45	45	%
Electrolyte	Weight	14	14	14	mg/cm ²
Gas diffusion layer	Weight	8.4	8.4	8.4	mg/cm ²
	Thickness	220	220	220	μm
	Porosity	89	89	89	%
Current collector	Weight	3.5	3.5	3.5	mg/cm ²
Gas diffusible current collector	Weight		1.3	1.3	mg/cm ²
Cu foil (10 μm)	Weight	8.8			mg/cm ²
	Thickness	10			μm
Cu foil (2 μm)	Weight		1.8	1.8	mg/cm ²
	Thickness		2	2	μm
Standard protective membrane	Weight	6.5	6.5		mg/cm ²
	Thickness	20	20		μm
Lightweight protective membrane	Weight			1.9	mg/cm ²
	Thickness			6	μm
Li foil (50 μm)	Weight	2.67	2.67	2.67	mg/cm ²
	Thickness	50	50	50	μm
Total weight		46.3	28.7	24.1	mg/cm ²
Average voltage		2.7	2.7	2.7	V
Areal capacity		6	6	6	mAh/cm ²
Areal electric energy					Wh/cm ²
Energy density		349	563	671	Wh/kg

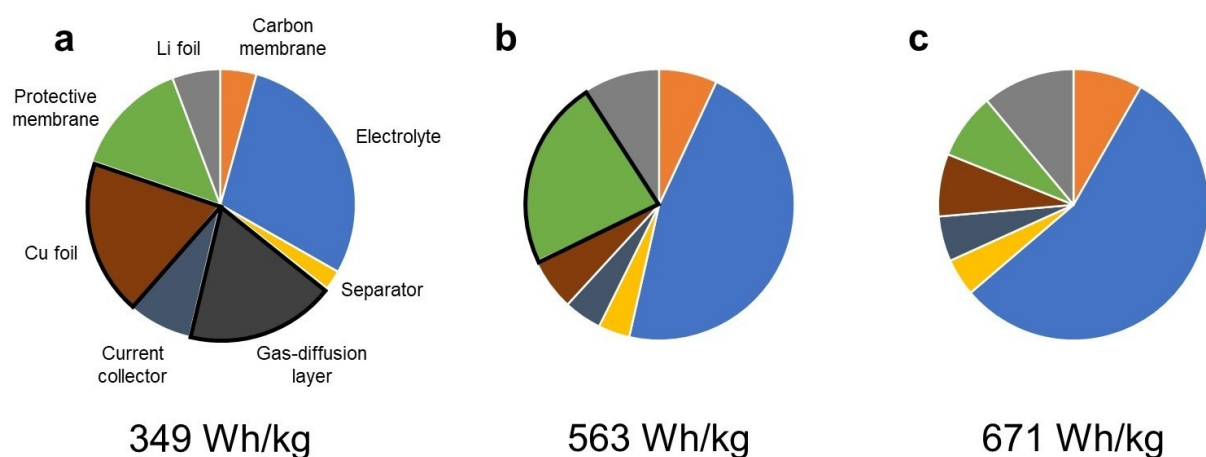


Figure 1. Weight fractions of LOB components calculated using the parameters listed in Table 1.

over of redox mediators. The impact of chemical cross-over becomes much more prominent in the case of an LOB cell designed to provide a high energy density, in which the distance between electrodes is reduced and the areal capacity is high. These features lead to the formation of greater amounts

of side products on the oxygen electrode side that subsequently pass through the negative electrode. In the majority of prior LOB studies, the distance between the negative and positive electrodes exceeded 100 μm because of the use of separators comprising thick glass fibers. In contrast, an LOB

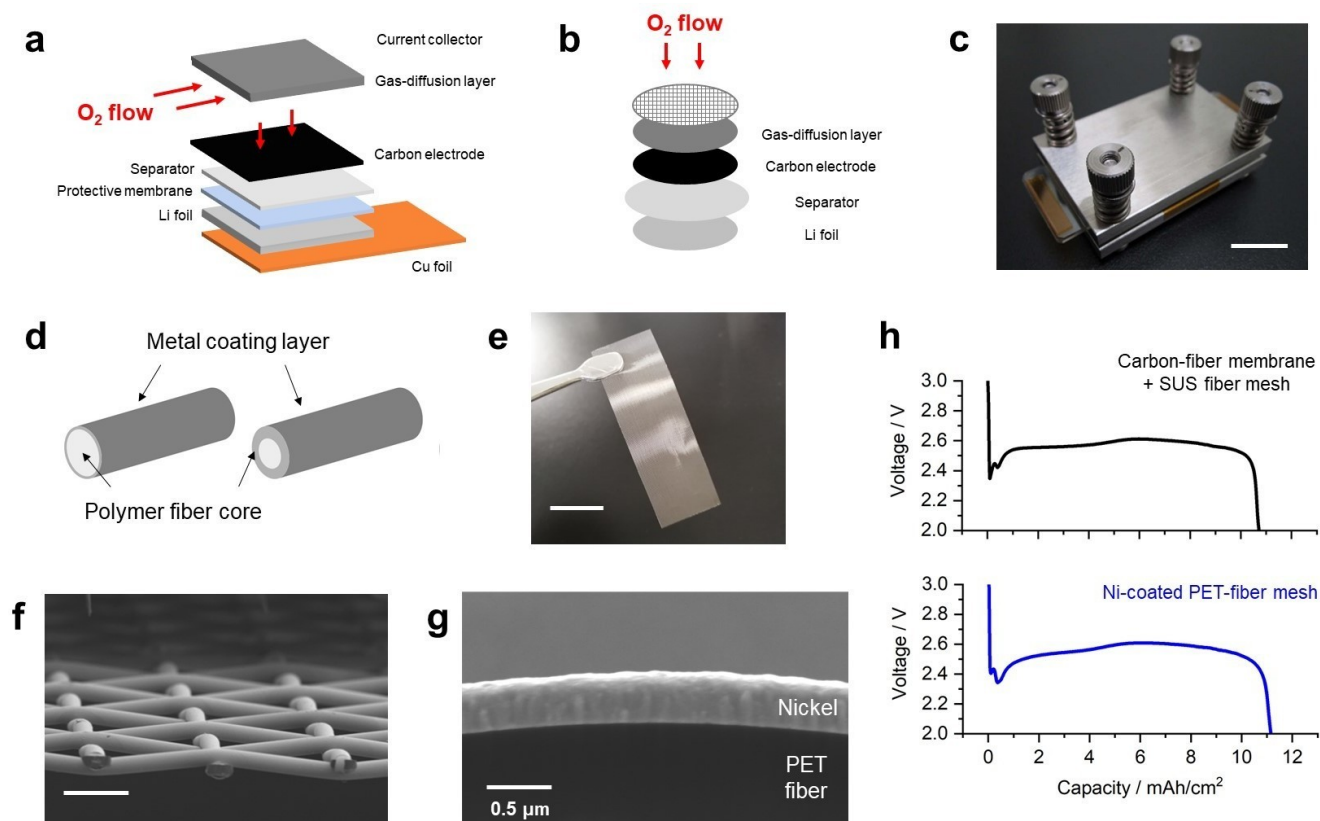


Figure 2. (a) Schematic illustration of LOB with stacked cell configuration. (b) Schematic illustration of LOB with coin-type cell configuration. (c) Photographic image of a single-layered LOB cell with a 2 cm \times 2 cm sized electrode. (d) Illustration of a metal-coated polymer fiber. (e) Photographic and (f, g) SEM images of Ni-coated PET fiber mesh. Scale bars are (c) 1 cm, (e) 2 cm (f) 100 μ m and (g) 0.5 μ m.

designed to produce a high energy density may include a thin separator and have an electrode distance of less than 20 μ m. Recent work using a three electrode setup was able to deconvolute the over-potentials associated with the positive oxygen electrode and negative lithium metal electrode and demonstrated that deterioration of the latter was the main reason for the limited cycle lifespan of an LOB having a high energy density.^[7] In addition, assessments using in situ mass spectrometry have established that the reaction efficiency of the lithium electrode decreases over time primarily because of the cross-over of compounds such as H₂O and CO₂ from the positive oxygen electrode side (Figure 3a). These compounds are considered to be generated as side products of solvent decomposition during positive electrode reaction.^[8–10]

To protect the lithium metal electrode from such undesirable products from the positive electrode side, the use of lithium-ion selective membrane as a separator is an effective approach. As an example, the use of a solid-state electrolyte based on LAPT can provide superior Li ion conductivity ($> 10^{-4}$ mS/cm²) and resistance to attack by chemical cross-over compounds. The concept of protecting a lithium metal electrode using an LAPT pellet was demonstrated by Visco et al.^[12] As described in Section 2.1, reducing the mass of the protective membrane applied to the lithium metal electrode without diminishing its protective ability is an essential aspect of producing LOBs with high cell-level energy densities.

Although a 20- μ m-thick LAPT pellet with a mass loading of 6.5 mg/cm² is commercially available from the Ohara Company, further reduction of weight and thickness of LAPT pellet is required. Recent studies have demonstrated the application of a 6- μ m-thick LAPT pellet for LOBs (Figure 3b). Notably, Li ion conductivity of this material is equivalent to that of standard thick LAPT pellet. The use of this 6- μ m-thick LAPT pellet as separator in 400 Wh/kg class LOB, the cycle life of LOB is largely improved over 20 cycle (Figure 3c), which is the best performances among the LOB reported so far, especially in the region of energy density higher than 200 Wh/kg.^[11]

As the lightweight flexible protective separator, the hybrid membrane made of micron-sized LAPT particles embedded in a polymeric matrix is also alternative candidate.^[13] The unique structure of the membrane enables both high Li-ion conduction and gas-impermeability (Figure 3d and 3e). Notably, by use of this membrane as separator, the operation of 500 Wh/kg class LOB was demonstrated, although its cycle life is not reported. The development of lightweight, flexible and scalable protective membranes for lithium metal electrodes is important to the future development of high-performance LOBs and further intensive studies are highly demanded.

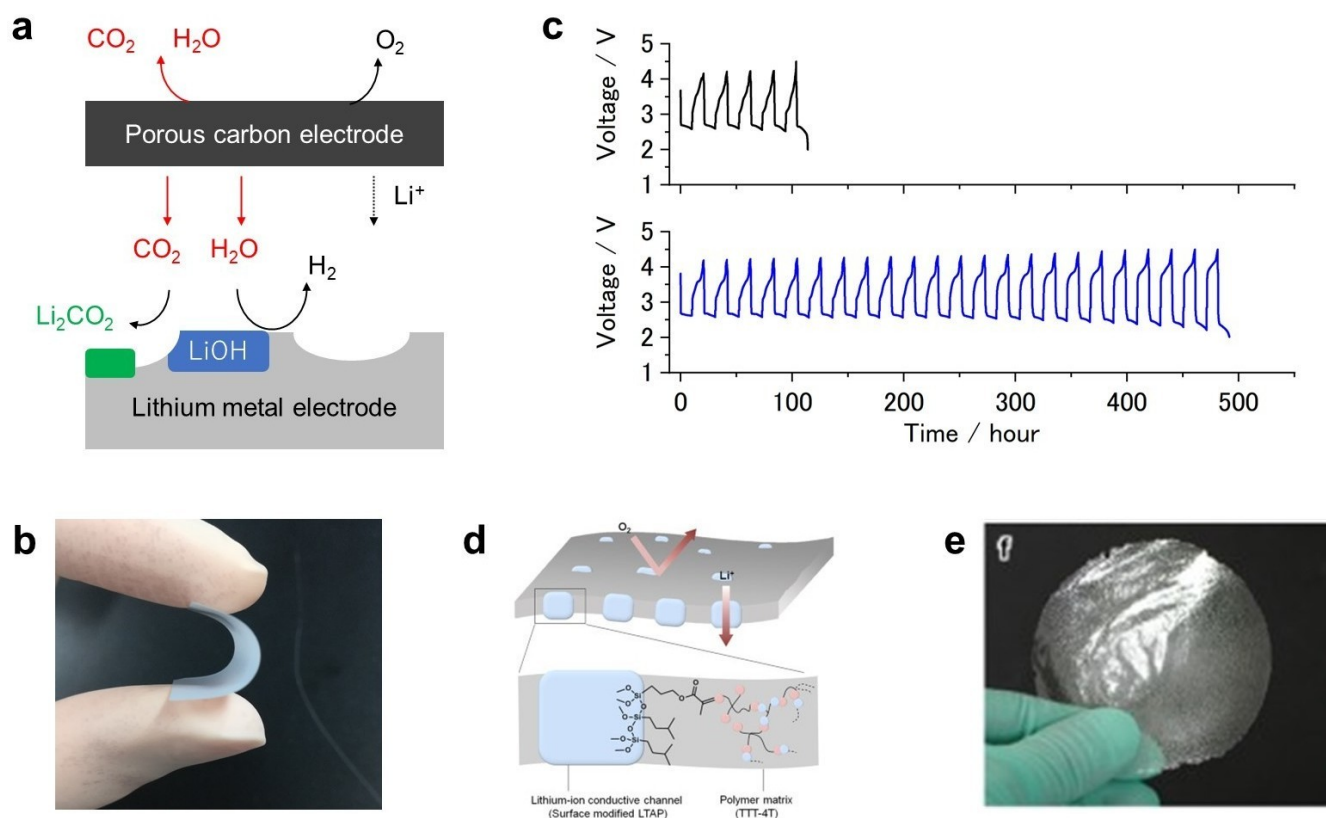


Figure 3. (a) schematic illustration of chemical cross-over phenomenon in LOBs. (b) Photographic image of 6- μm -thick Li conductive solid-state ceramic-based separator (2 cm in square). (c) Discharge/charge profiles of the LOB with (blue) and without (back) the lightweight solid-state ceramic-based separator. (d) Schematic illustration of the membrane with aligned lithium-ion conducting channel. (e) Photographic image of ion-channel aligned membrane (8 cm in diameter).

3. Physical degradation mechanisms

3.1. Electrode Volume Changes

In LOBs, both chemical and physical degradation processes can occur. Importantly, the reactions in LOBs proceed on the basis of the formation or decomposition of active solid-state compounds (specifically, Li_2O_2 in the positive electrode and Li metal in the negative electrode). As such, the electrode volume change in an LOB will be much larger than that in a standard LiB, which operates via an intercalation mechanism. Considering the fact that the volume change of the active material in LiB has a large impact on the cycle life, the correct understanding of how the volume change of the electrode occurs in LOB is crucial for the design of materials that realize the LOB with long cycle life. Typically, the performance of LOBs is evaluated under low areal capacity conditions ($< 1 \text{ mAh/cm}^2$). In such cases, the amount of Li_2O_2 that is formed and decomposed during discharging and charging, respectively, is relatively small ($< 0.5 \text{ mm}^3/\text{cm}^2$). Thus, the impact of electrode volume changes is minimal. Conversely, LOBs exhibiting high cell-level energy densities also demonstrate high areal capacity values ($> 4 \text{ mAh/cm}^2$). Consequently, the reversible formation and decomposition of large amounts of Li_2O_2 ($> 1 \text{ mm}^3/\text{cm}^2$) can have a significant effect on the porous carbon electrode. In such high-

energy-density LOB cell, the electrode materials (porous carbon positive electrode and lithium metal negative electrode) after long cycle test can be easily damaged during cell disassembling and sample washing process. Therefore, non-destructive techniques play a crucial role in acquiring quantitative information about the volume change of electrodes.

Recently, X-ray computed tomography (X-ray CT) has been applied as a very promising nondestructive observation method that can provide three-dimensional imaging of samples by irradiation with an X-ray beam from different directions, and the use of XCT analysis of the LOBs were reported.^[14–16] Figure 4a and 4b shows the cross-sectional XCT images of the LOB cell before and after 10th cycles. Associated with the progress of 10th cycles, there can be seen the largely volume change of electrodes. For negative electrode, thickness increased from 50 to 180 μm , a greater than 3-fold difference. In contrast, the positive electrode thickness decreases from 160 to 75 μm . As a constant pressure was maintained in the cell, this decrease can be attributed to the compression of the porous carbon membrane owing to the corresponding increase in the negative electrode thickness. Overall, the XCT analysis images provide crucial information on the evolution of deposit formation and the corresponding electrode volume changes over multiple discharge/charge cycles, thereby demonstrating

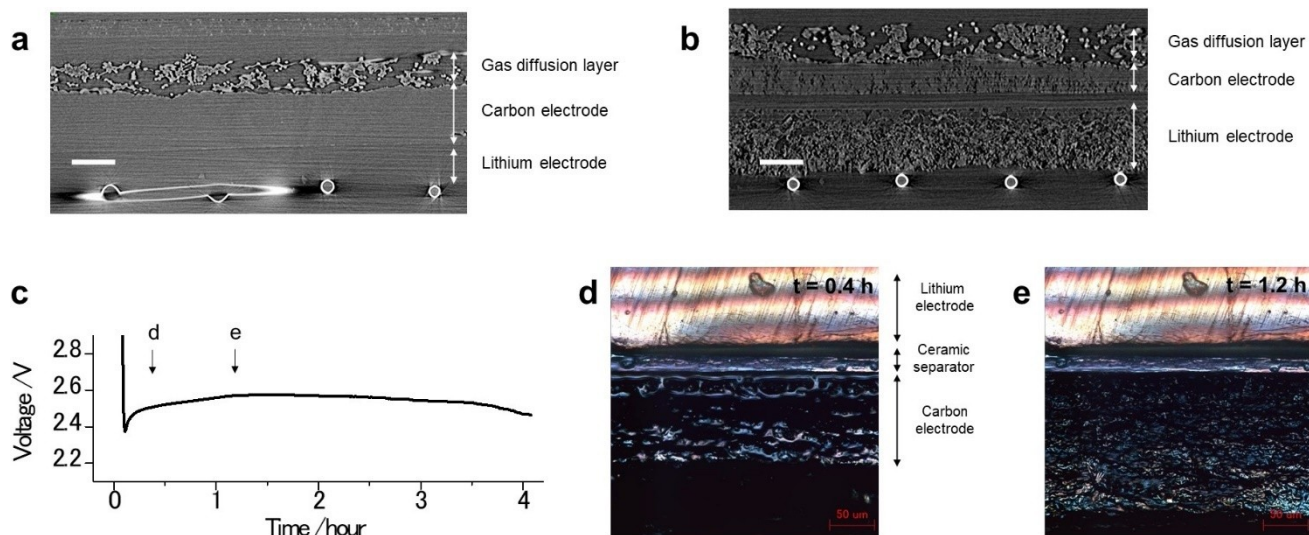


Figure 4. XCT images of the LOB cell (a) before cycling and (b) after the 10th discharge/charge cycle. (c) Voltage profile of LOB cell for confocal microscopic analysis. (d, e) Cross-sectional confocal microscopy images of a fabricated LOB cell taken at various time intervals during the discharge process.

the utility of this technique for studying physical changes in the LOB components.

Confocal microscopy is also effective technique for analyzing the volume change of electrodes in LOBs in non-destructive manner. A prior study by the present authors using operando confocal microscopy confirmed a very large change in the volume of the porous carbon electrode during discharge under high current density conditions ($>1 \text{ mAh/cm}^2$).^[14] In these experiments, the cell voltage abruptly dropped to 2.4 V and then gradually increased to 2.55 V (Figure 4c), which is considered to be originated in the increase of effective electrochemical surface area by formation of Li_2O_2 on the electrode. Following this, the discharge voltage gradually decreased to the areal capacity limit. Notably, a considerable volume change was observed in the positive electrode over the duration of the discharge, with an increase in thickness from 110 to 250 μm by the halfway point of the process (Figures 4d and 4e). In this work, a self-standing, binder-free, single-walled carbon nanotube (CNT) membrane was utilized as the carbon electrode. Because this membrane was prepared via a simple vacuum filtration method, the CNT fibers were not strongly connected to one another. During discharge under high current density conditions, the concentrations of oxygen and lithium ions rapidly decreased as the oxygen reduction reaction proceeded at the electrode. In addition, Li_2O_2 was formed at localized sites on the electrode, inducing macroscopic expansion of the carbon electrode. This inhomogeneous process could explain the sudden change in the electrode volume. For this reason, the porous carbon must possess sufficient mechanical properties to resist variations in volume during repeated discharge/charge cycles. The complex reactions occurring in LOBs have not yet been fully explored, especially in the case of cells designed to provide high energy densities. An improved understanding of the complicated phenomena associated with

these devices is therefore crucial to establishing principles for the design of electrode materials.

3.2. Electrolyte Movement Phenomenon

Electrolyte movement phenomenon is another physical degradation mechanism unique to LOBs having high cell-level energy density designs. If the available pore volume in the carbon electrode is completely filled with electrolyte, a portion of the electrolyte will be forced out as Li_2O_2 is formed during discharge, assuming that the electrode volume does not change. This phenomenon has been demonstrated experimentally using cross-sectional confocal microscopy.^[14] Research has confirmed the formation of electrolyte droplets on the carbon electrode during discharge. Following this, as charging occurs, these droplets are absorbed back into the electrode. In addition to this electrolyte movement in the horizontal direction, a similar process is believed to occur in the vertical direction. In such cases, the electrolyte can migrate to the negative lithium electrode and/or GDL. The latter has a large volume that can accommodate a significant amount of electrolyte, and so some of the electrolyte may not return to the carbon electrode during charging. Although study for experimental confirmation of electrolyte depletion is limited, several studies have suggested that this is possible.^[17,18] As an example, a sudden increase in voltage during the initial part of the charging process has been observed in trials with an LOB incorporating a lean electrolyte and with a high areal capacity.^[19,20] Notably, replacing the conventional carbon fiber GDL with a hydrophobic poly(tetrafluoroethylene) layer suppresses increases in the charging voltage. These results suggest that interactions between the GDL and the electrolyte can modify the charging voltage profile. Ideal GDL materials should therefore be hydrophobic and lightweight.

4. Summary and Outlook

This article provided an overview of future research trends related to the development of GDLs for efficient oxygen transport and protective membranes for lithium metal electrodes. Although there has been limited research to date concerning these materials compared with work related to porous carbon electrodes and electrolytes, the development of these components is crucial to the realization of LOBs exhibiting energy densities suitable for practical applications. Although the details are not mentioned in this article, the development of oxygen permeable membrane is also crucial for realizing practical LOBs.^[21] This article also highlighted the importance of physical degradation phenomena in LOBs, which should also be taken into account when attempting to prolong the cycle life. As an example, a case study examining volume changes of the positive electrode and movement of the electrolyte was presented. Both degradation mechanisms are unique to LOBs. Despite work to date, additional knowledge concerning the complicated degradation mechanisms occurring in LOBs is needed, based on the use of non-destructive analytical techniques. Such information is thought to be vital to the development of LOBs with long cycle life.

Conflict of Interests

The authors declare no conflict of interest.

Data Availability Statement

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

Keywords: Metal-air batteries · Volume change · Energy conversion · Electrochemistry

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Manuscript received: October 29, 2023

Revised manuscript received: December 26, 2023

Version of record online: January 22, 2024