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A new perspective of the ruthenium ion: a bifunctional soluble catalyst for high efficiency Li–O₂ batteries†

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The slow kinetics of Li–O₂ batteries cause a large overpotential, which leads to low round-trip efficiency and poor cyclability. Applying a suitable bifunctional catalyst can be an effective way to solve this problem. We anticipated that the ruthenium ion dissolved in the electrolyte will not only overcome the disadvantages of solid phase catalysts, but also reduce the overpotential for both charge and discharge. This is possible due to the suitable redox potential of the ruthenium ion, which effectively reduced the oxygen evolution reaction (OER) overpotential, and the affinity between the ruthenium ion and oxygen, which facilitated the oxygen reduction reaction (ORR) and suppressed the degradation of the cathode. Here, we propose a new soluble catalyst, ruthenium bromide, for Li–O₂ batteries. The battery using ruthenium bromide clearly exhibited enhanced cycling performance, increasing round-trip efficiency (from 68.2% to 80.5%) and rate capability. A new understanding and application of the soluble ruthenium catalyst, which is commonly used as a solid catalyst, will not only overcome the existing problems but also provide a promising platform for Li–O₂ batteries.

Due to the continuing depletion of fossil fuels and global warming, the need for eco-friendly energy is increasing worldwide, which requires suitable energy storage and conversion devices. In accordance with the above purpose, Li-ion batteries have already been successfully applied to portable electronic devices and power tools. However, they encounter a theoretical limit for energy density, which is not enough to achieve the demand of emerging energy markets for EVs. As one of the candidates for next generation energy storage systems, Li–O₂ batteries are attracting much attention because of their extremely high theoretical energy density (3500 Wh kg^{−1}, on the basis of Li₂O₂), which is several times higher than that of conventional Li-ion batteries (250 Wh kg^{−1}).^{1,2}

However, several issues have obstructed the practical application of Li–O₂ batteries. The slow reaction kinetics in Li–O₂ batteries cause a large overpotential, which leads to not only low round-trip efficiency, but also parasitic reactions. Moreover, the accumulation of insulating lithium peroxide (the main discharge product) on the electrode surface during cycling tests blocks the electron and oxygen pathways, resulting in deterioration of battery cyclability.

To overcome these drawbacks, various catalysts have been explored.^{3–7} However, the catalytic activity of most solid catalysts is degraded very quickly during cycling tests because the immovable solid catalysts covered with accumulated discharge products and by-products cannot affect additional discharge products. Over the last several years, many mobile soluble catalysts have been adapted to solve the problems of solid catalysts. The soluble catalyst, which is contained in the electrolyte, is first oxidized during the charging process and reacts with the discharge product to facilitate reversible decomposition. Because of this charge carrying principle, a soluble catalyst is also called a redox mediator (RM).^{8–20} RMs have been applied to Li–O₂ batteries, exhibiting excellent electrochemical performance.

The oxygen reduction reaction (ORR, discharge) is as important as the oxygen evolution reaction (OER, charge) because the characteristics of the discharge product significantly affect the OER. Nevertheless, only a few soluble catalysts (e.g., FePc (iron phthalocyanine), Heme molecule) that exhibit catalytic effects for both the OER and ORR have been reported.^{11,16} However, these reported bifunctional soluble catalysts leave much to be desired. First, these catalysts have a very high probability of decomposition in the harsh environment of Li–O₂ batteries because of their chemical structure. These catalysts exist as metal ion-containing forms in very large organic molecules. Additionally, the redox potentials of bifunctional RMs are comparatively slightly higher than those of others, which cannot effectively increase the round-trip efficiency of Li–O₂ batteries.

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Here, we suggest a new understanding and application of a suitable soluble bifunctional catalyst, RuBr_3 , for Li-O_2 batteries. The ruthenium ion is expected to be a suitable RM for the OER in Li-O_2 batteries because its redox potential is 3.28 V (vs. Li/Li^+),²¹ which is slightly higher than the potential of formation and decomposition of Li_2O_2 . Simultaneously, the ruthenium ion is also expected to facilitate the ORR during discharge due to the affinity between the ruthenium ion and oxygen. According to previous research, the affinity between the ruthenium ion and oxygen is the driving force of the catalytic effect when using ruthenium or ruthenium oxide as a solid catalyst for Li-O_2 batteries. We believe that this affinity can even act in a liquid state. We sought an appropriate ruthenium compound to obtain both catalytic effects with stable operation. Thus, ruthenium bromide (RuBr_3) is selected and applied to Li-O_2 batteries as a soluble catalyst to reduce the OER and ORR overpotentials.

We investigated the electrochemical catalytic effect of RuBr_3 using cyclic voltammetry (CV). In Fig. 1a, we can find two small peaks in the CV results, which are related to the ORR and OER of Li-O_2 batteries under an oxygen atmosphere using the normal electrolyte, *i.e.*, 1 M LiTFSI in DMSO without a soluble catalyst. In contrast, the Li-O_2 battery prepared using the electrolyte containing RuBr_3 exhibits two comparatively large peaks in both the cathodic and anodic scans. To distinguish these peaks, a CV test with a Li-O_2 battery prepared using the electrolyte containing lithium bromide (LiBr) is performed under an oxygen atmosphere with the same test conditions. As shown in Fig. 1a (blue line), the reduction and oxidation peaks appeared at 3.5 V and 3.72 V, respectively. These results agree with those of a previous report.¹⁰ We infer that the peaks at 3.24 V (oxidation) and 3.0 V (reduction) from the electrolyte containing RuBr_3 are related to electron transfer between ruthenium and the cathode. The Li-O_2 battery prepared using

the electrolyte containing RuBr_3 exhibited both a higher current and initial voltage for the ORR compared to those using the electrolyte containing LiBr and the electrolyte without a RM (under 2.75 V). These results demonstrate that RuBr_3 improves both the OER and ORR.

To understand the practical advantage of the ruthenium ion, we also executed galvanostatic testing of the Li-O_2 batteries. In order to characterize the catalytic properties of the ruthenium ion alone, commercial carbon paper (SGL group, BC35), which does not contain any solid catalyst, was used as a cathode. The Li-O_2 batteries were tested under the capacity limit conditions (0.52 mAh cm^{-2}) using the electrolyte 1 M LiTFSI in DMSO with/without RuBr_3 , and we found three notable advantages. First, as shown in Fig. 1b and d, RuBr_3 clearly reduces the OER overpotential. To clarify the catalytic effect of the ruthenium ion, we also tested the Li-O_2 batteries with 0.3 M LiBr + 1 M LiTFSI in DMSO as a reference electrolyte because the bromide anion is known as an effective redox mediator in Li-O_2 batteries.^{11,15} The catalytic effect of the ruthenium ion, besides the catalytic effect of the bromide anion, could be demonstrated when the electrolytes are compared with the same concentration of the bromide anion. For this reason, as shown in Fig. 1c, we choose 0.3 M LiBr + 1 M LiTFSI in DMSO as a reference electrolyte which has the same concentration of the bromide anion as the RuBr_3 added electrolyte (0.1 M RuBr_3 + 1 M LiTFSI in DMSO). The lower plateaus (3.16 V) of charge for the RuBr_3 added electrolyte disappeared when LiBr was used, as shown in Fig. 1c and d. These results demonstrate that the catalytic effect of lower plateaus (3.16 V) during charge came from the Ru species. In addition, the shortage of the RM causes the appearance of a second plateau at 3.73 V.⁹ This phenomenon is a result of the fact that RuBr_3 is not very soluble in organic solvents even though we used DMSO, which has a high dielectric constant (47.24 at 20 °C). To understand the concentration effect of RuBr_3 , the galvanostatic cycling test results of Li-O_2 batteries using the same conditions except lower concentrations of RuBr_3 (0.01 M and 0.05 M) were evaluated (Fig. S1†). Similar to the results of preceding research studies dealing with the concentration of redox mediators, a higher concentration of RuBr_3 exhibited better performance of Li-O_2 batteries with a lower charge overpotential. Second, the voltage profile also indicates that RuBr_3 acts as both an OER and ORR catalyst. The ORR overpotential of the RuBr_3 added electrolyte is 50 mV lower than those of the other electrolytes, and this phenomenon corresponded to the cyclic voltammetry results discussed above. The RuBr_3 added electrolyte successfully reduces the overpotential of both the OER and ORR. Eventually, the RuBr_3 added electrolyte increases the round-trip efficiency of Li-O_2 batteries from 68.2% to 80.5%. Fig. 1a also indicates a lower overpotential for both the OER and ORR of the RuBr_3 added electrolyte than those of the other electrolytes. Finally, the cyclability of the RuBr_3 added electrolyte is improved compared to the other electrolytes (electrolyte using LiBr and electrolyte without a RM). In the case of the Li-O_2 battery using the electrolyte with LiBr added, the OER overpotential rapidly increased starting from the 8th cycle, and then the cell failed at the 15th cycle. In contrast, the cell using the electrolyte containing RuBr_3

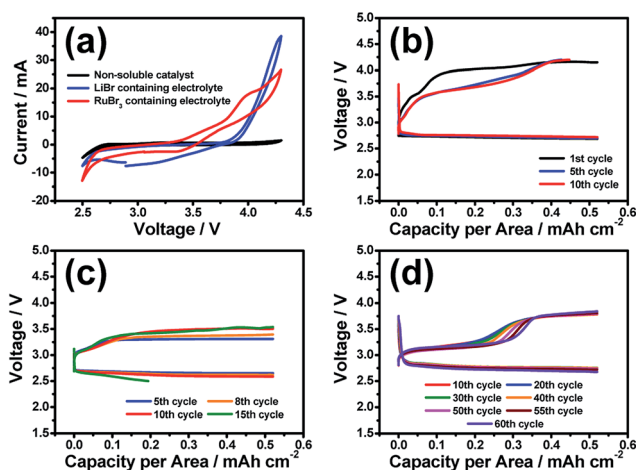


Fig. 1 (a) Cyclic voltammetry behavior of Li-O_2 batteries under an oxygen atmosphere using different electrolytes: 1 M LiTFSI in DMSO (black line), 0.3 M LiBr + 1 M LiTFSI in DMSO (blue line), and 0.1 M RuBr_3 + 1 M LiTFSI in DMSO (red line). Galvanostatic behavior of Li-O_2 batteries using different electrolytes: (b) 1 M LiTFSI in DMSO, (c) 0.3 M LiBr + 1 M LiTFSI in DMSO, and (d) 0.1 M RuBr_3 + 1 M LiTFSI in DMSO.

showed comparatively stable charge and discharge profiles until the 60th cycle.

To demonstrate the reversibility of forming and oxidizing Li_2O_2 , we performed *ex situ* characterization of the electrodes after charge and recharge *via* X-ray diffraction (XRD) and scanning electron microscopy (SEM). As shown in Fig. 2, the SEM images demonstrate that micron-sized discharge products are formed upon discharge and are clearly decomposed upon charge. With XRD characterization, only the formation and decomposition of Li_2O_2 are clearly confirmed during cycling. Moreover, as shown in Fig. S3,† Li_2O_2 is reversibly formed and decomposed on the cathodes after 10th and 30th cycles (discharge/charge). Meanwhile, Li-metal anodes in the same cells after 10th and 30th cycles were found to be stable (Fig. S4†). This result proves that RuBr_3 does not affect the chemistry of the discharge product although it facilitates both the OER and ORR.

The rate capability tests are also performed with diverse current densities, as shown in Fig. 3. It is worth noting that the polarization was not significantly large and that cyclability was maintained, though the current density was increased three times because soluble catalysts are less affected by current density than solid catalysts, owing to their mobile characteristics. These results also confirm our expectation that RuBr_3 effectively acts as a catalyst in liquids.

The catalytic effect of RuBr_3 is distinct from those of typical redox mediators for increasing the efficiency of Li– O_2 batteries. As mentioned above, RuBr_3 shows the catalytic effect for not only the OER, but also the ORR. We found a possible explanation leading to a new understanding of the ruthenium ion as an ORR catalyst in a previous report.^{22–24} Ruthenium or ruthenium oxide has already been identified as a solid catalyst in Li– O_2 batteries by preceding research. According to the preceding results, the driving force of the catalytic effect is the affinity of ruthenium and ruthenium oxide for the oxygen molecule. We believe that a chemical or physical interaction between the ruthenium ions and the oxygen molecule can act even in a liquid state. Therefore, to demonstrate the change of the ruthenium ion state through coordination with oxygen, ultraviolet-visible spectroscopy (UV-Vis) was performed. As shown in Fig. 4a, a broad absorption peak appeared between

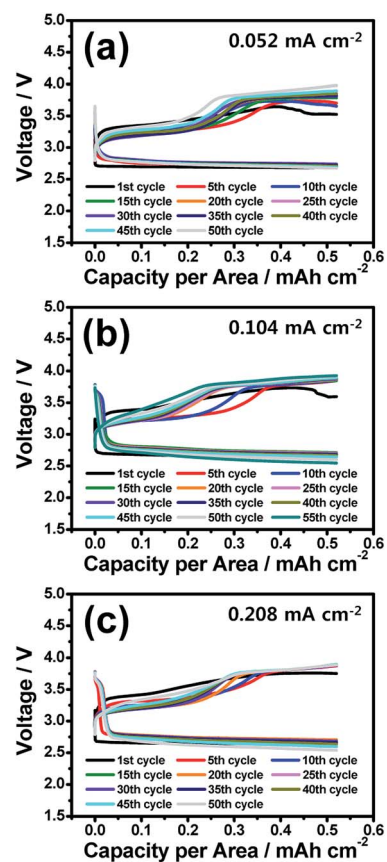


Fig. 3 Galvanostatic results of Li– O_2 batteries at the same capacity with different current densities: (a) 0.052 mA cm^{-2} with a 10 h time limit, (b) 0.104 mA cm^{-2} with a 5 h time limit, and (c) 0.208 mA cm^{-2} with a 2.5 h time limit.

400 nm and 650 nm when the electrolyte containing RuBr_3 was measured by UV-Vis, whereas no peaks are observed in the case of the electrolyte without RuBr_3 or the DMSO solvent. Therefore, we confirm that the peak detected between 400 nm and 650 nm corresponds to ruthenium. To demonstrate the interaction between oxygen and the ruthenium ion, comparative UV-Vis spectra were examined by using the electrolyte containing RuBr_3 before and after oxygen gas bubbling for 30 min. Surprisingly, a red-shift occurs just after oxygen bubbling in the RuBr_3 added electrolyte. This result demonstrates a change in the state from Ru^{3+} to $\text{Ru}^{2+}\text{-O}_2$, which is similar to previous studies of UV-Vis spectra using Heme or FePc as bifunctional RMs for Li– O_2 batteries. Therefore, when RuBr_3 is used as a RM, a decrease of the ORR overpotential results from the interaction of Ru^{2+} and oxygen.

Previous studies have suggested that the solvated complex between potassium ions and oxygen is potentially stabilized for the formation of the lithium superoxide.²⁵ This property tends to form discharge products near the interface between the electrode and the electrolyte during the discharge process. Similarly, the interaction between ruthenium ions and oxygen will stabilize the superoxide, and discharge products will be formed mainly at the interface between the electrode and the

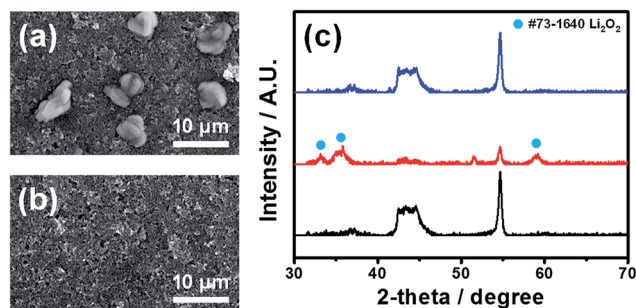


Fig. 2 SEM images of the (a) discharged and (b) charged cathodes using $0.1 \text{ M RuBr}_3 + 1 \text{ M LiTFSI}$ in DMSO electrolyte. (c) X-ray diffraction patterns before (black line) and after discharge (red line), and after recharge (blue line).

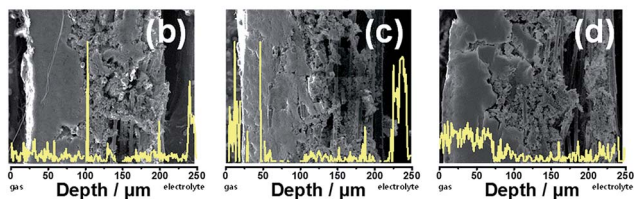
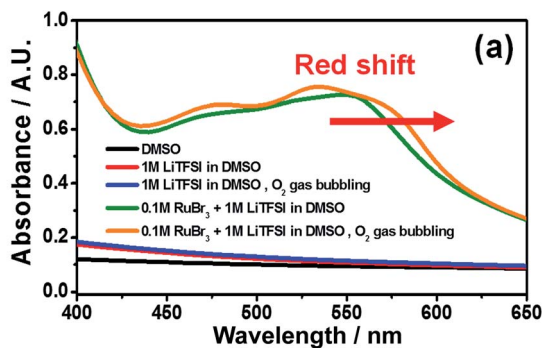


Fig. 4 (a) UV-Vis spectra of the electrolyte and oxygen-bubbled electrolytes. Cross-sectional SEM image and EDX results of the electrode after discharge with different electrolytes: (b) 1 M LiTFSI in DMSO, (c) 0.3 M LiBr + 1 M LiTFSI in DMSO, and (d) 0.1 M RuBr₃ + 1 M LiTFSI in DMSO. The yellow graph indicates the oxygen content. The right side is the gas/electrode interface and the left side is the electrolyte/electrode interface.

electrolyte. SEM and energy dispersive X-ray spectroscopy (EDX) were conducted on the cross-section of the cathode after discharge using electrolytes with LiBr, RuBr₃, and without a RM. As we expected, the ruthenium ion encourages the formation of discharge products near the electrolyte–electrode interface. In contrast, as a result of using the pristine electrolyte without a RM and the electrolyte with LiBr added, discharge products are formed at the air–electrode interface or both interfaces. The SEM images also clarify the ruthenium ion and oxygen interaction. We confirm that RuBr₃ as a RM not only reduces the ORR overpotential, but also maintains the oxygen pathway able to increase the lifetime characteristics of the Li–O₂ battery. DMSO, one of the electrolyte solvents that is known to be suitable for operating Li–O₂ batteries, promotes the solution mechanism during discharge, and thus shows a high discharge capacity.²⁶ However, without a RM, it is difficult to completely decompose Li₂O₂ during charging because the non-contacted site of toroidal Li₂O₂ is isolated from the cathode surface, and this residual is difficult to decompose. The residual discharge product accumulates on the surface of the electrode as the cycle progresses, thereby deteriorating the cycle life of the battery. However, when using electrolytes containing RMs, the non-contacted Li₂O₂ is easily decomposed by the mobile RM in the electrolyte without the formation and accumulation of residue on the electrode surface.^{10,12,13,16–20} Moreover, compared to the film-type Li₂O₂ in low DN solvent, toroidal Li₂O₂ in high DN solvent (DMSO) can react with the RM more frequently, which helps the RM effect for the OER in the Li–O₂ battery.

Therefore, we believe that finding a suitable soluble catalyst for the DMSO solvent is most important. Similarly, RuBr₃, which is an appropriate catalyst in DMSO, is worthy of

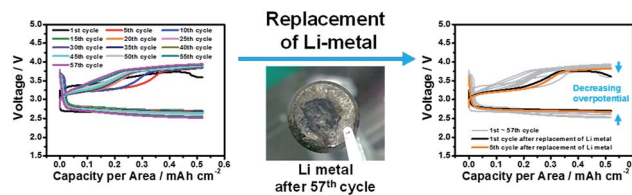


Fig. 5 Cycling test at the 57th cycle (left) and re-test (right) of the Li–O₂ battery after replacing the Li metal.

attention. The suitable redox potential of ruthenium ions makes them an OER catalyst in Li–O₂ batteries. Forming a complex of the ruthenium ion and oxygen reduces the ORR overpotential. Moreover, the formation and decomposition of discharge products at the electrode and electrolyte interface help to maintain the oxygen pathway as the cycle proceeds. Despite these advantages, due to the low solubility of RuBr₃ in ether solvents, DMSO having a high dielectric constant was used as a solvent, which is the main reason for the corrosion of lithium metal.²⁷ Although the overpotential increased during the cycling test with the electrolyte containing RuBr₃, the resistance decreased again when the lithium metal anode was changed, as shown in Fig. 5.

Experimental

Fabrication and electrochemical testing of Li–O₂ batteries

A homemade cell type was used, which consisted of a Teflon body squeezed between stainless steel plates. Dried commercial carbon paper (SGL group, BC35) and Li-metal were used as the cathode and the anode, respectively, and were separated by a glass fiber separator. The electrolyte was 1 M LiTFSI in DMSO with or without different soluble catalysts. All catalysts and LiTFSI were used after vacuum drying in a vacuum glass oven (Buchi, B-585) for more than 48 hours at 120 °C. The DMSO solvent was further purified using a vacuum-dried molecular sieve (4 Å, Sigma Aldrich). The water content of the electrolytes did not exceed 20 ppm as a result of titration using a C 20 coulometric KF titrator (Mettler Toledo). The electrodes and separators were used after vacuum drying (Buchi, B-585, 110 °C, 72 hours). In addition, the cell was assembled in an argon gas purged glove box (0.1 ppm H₂O, 0.1 ppm O₂). Galvanostatic measurements were performed at 0.052 mA cm⁻² with a constant current. All the measurements were carried out using a VMP3 system from Bio-Logic.

Characterizations

After being charged and recharged, the electrodes were observed *via* high resolution XRD (9 kW, SmartLab, Rigaku) with Cu K-alpha radiation, field emission SEM (S-4800, Hitachi), and an ultraviolet-visible spectrophotometer (Lambda 650S, Perkin Elmer), these instruments are installed at Hanyang Center for Research Facilities (Seoul). All samples were cleaned with DMSO, dried, and sealed in an Ar-filled glove box. The samples for XRD were prepared using PI (polyimide) tape. The

oxygen-bubbled electrolyte was prepared at room temperature and humidity (20–22 °C, dew point - 60 or less).

Conclusions

In summary, the new soluble catalyst RuBr₃ demonstrated the bifunctional soluble catalytic effect for both the OER and ORR in Li–O₂ batteries. RuBr₃ reduces the OER overpotential *via* the suitable redox potential of Ru³⁺ and Ru²⁺ (3.28 V), which is slightly higher than the formation and decomposition potential of Li₂O₂ (2.97 V). In addition, the ORR overpotential is 50 mV lower than those of other electrolytes due to the interaction of Ru²⁺ and oxygen. We clarify this interaction using the UV-Vis spectra. This interaction not only reduces the ORR overpotential, but also increases the cyclability by securing the oxygen and electron pathway. Moreover, the smaller-sized ruthenium ion (compared to other RMs) is suitable for the harsh Li–O₂ battery environment. The batteries using RuBr₃ showed a high round-trip efficiency (80.5%) with stable cyclability (up to the 60th cycle). We believe that our study provides a promising platform to choose soluble catalysts for Li–O₂ batteries.

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