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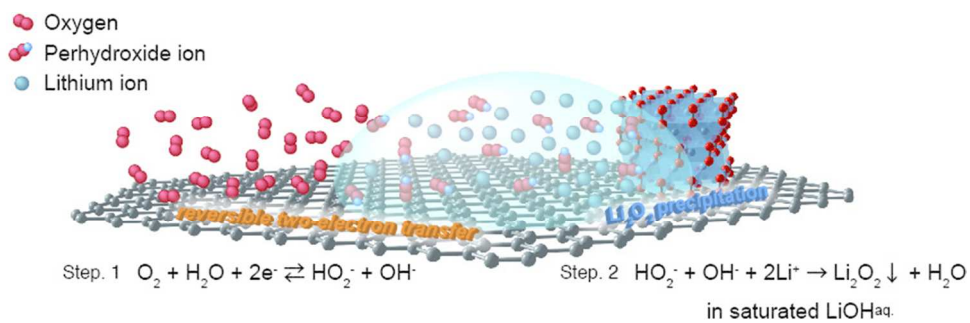


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COMMUNICATION

A novel aqueous lithium-oxygen cell based on oxygen-peroxide redox couple

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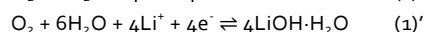
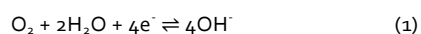
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The electrochemical process of an aqueous Li-O₂ cell is investigated. A Li₂O₂ is detected as a discharging product of an aqueous Li-O₂ cell using a catalyst-free carbon-based electrode. The electrolyte solution saturated with lithium hydroxide prevents the hydrolysis of the Li₂O₂. Since the electron transfer process is based on the oxygen-peroxide redox couple, the galvanostatic charging-discharging profile shows stable cycling with extremely low charging overpotential < 0.1 V at 1.0 mAcm⁻².

Recent advances in electrical energy storage have been getting more interests to realize the future sustainable society. Since the specific energy of state-of-art lithium ion batteries is getting close to the theoretical limit, breakthroughs in new battery chemistries are strongly expected¹. Li-O₂ system is the most promising battery chemistry owing to its high theoretical energy density². Hence a lot of studies have been carried out after the 1st report of Abraham et al.³ and the 1st experimental confirmation of the reversibility performed by Bruce et al.⁴. The biggest challenge in the non-aqueous Li-O₂ system is the extremely large overpotential⁵. The total polarization between discharging and charging process reaches >1 V, even in the case of best one ever reported⁶.

An approach for the improvement in the power density of the Li-O₂ battery is utilization of oxygen reduction process in aqueous media⁷. In the aqueous system, the electrochemical reaction at the gas-diffusion electrode is based on oxygen-water couple described in the following equations.



This reaction shows much lower overpotential than the non-aqueous system, however the aqueous system still needs catalysts both for the

oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER). Therefore, a lot of bi-functional catalyst materials have been investigated for a long time, regarding rechargeable zinc-air battery applications⁸. Another problem of the aqueous Li-O₂ battery is water consumption during the oxygen reduction process. Since the excess electrolyte solution needs to be confined in the cell, the energy density of the aqueous system needs to be sacrificed.

Here we introduce preliminary results of a novel electrochemistry for the aqueous Li-O₂ battery based on oxygen-peroxide couple using a catalyst-free carbon-based electrode, showing extremely low over potential for OER.

The gas-diffusion electrode was prepared by mixing a carbon black and polytetrafluoroethylene (PTFE) binder to form a sheet, and then the sheet was layered with a carbon paper. The electrochemical measurement was performed using a conventional three-electrode cell equipped with Ag/AgCl reference electrode and Pt / Pt-black counter electrode. Considering the stability of the solid-state electrolyte, we chose the aqueous electrolyte solution having 10 M LiCl and saturated with LiOH·H₂O⁹. After the electrochemical tests, the electrodes were carefully rinsed with anhydrous ethanol in inert atmosphere and dried, subsequently analyzed using scanning electron microscope (SEM) and X-ray diffraction (XRD). The structural refinement was performed using RIETAN-FP¹⁰. The detailed experimental conditions are provided in the electrical supplementary information.

Fig. 1 shows an XRD pattern and an SEM image of a gas-diffusion electrode after a galvanostatic discharging process. Surprisingly the refined XRD pattern well matched with the simulated diffraction pattern of the Li₂O₂: PDF01-074-0115. All the other diffraction peaks are corresponding to either the carbon paper or the aluminium sample holder. Typically the hydrolysis of the Li₂O₂ takes place in the aqueous electrolyte solution as shown in the following equation.

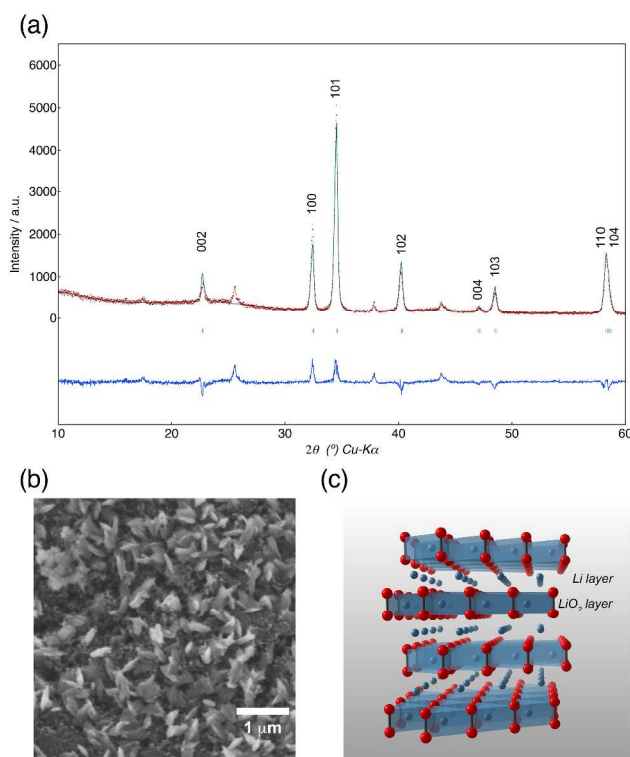
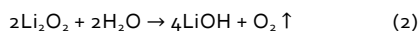


Fig. 1 Structural characterization of the discharged electrode. A powder XRD pattern of the electrode after 50 hours of a discharging process (a). The refined XRD pattern shows a measured diffraction pattern (brown), a simulated pattern (green) and residuals (blue). An SEM image of the discharged electrode (b) and a crystal structure of the lithium peroxide (c)



However since the electrolyte solution is saturated with the LiOH, the hydrolysis of the Li_2O_2 seems to have been prevented. The sharp diffraction peaks show that the formation of the highly crystalline Li_2O_2 compared with the discharging products of the non-aqueous $\text{Li}-\text{O}_2$ batteries reported in the past^{5b, 11}. It indicates the formation process of the Li_2O_2 in the present system is not equal to the non-aqueous system. Fig. 1 (b) shows the SEM images for the air electrodes. The flake-like deposits observed at the surface of the electrode could be reflecting the crystal structure of Li_2O_2 (Fig. 1(c)). The submicron-sized Li_2O_2 particles are also reasonable to explain the high crystallinity of the Li_2O_2 discussed in the XRD. The bond length of two oxygen atoms in the LiO_2 layer: approx. 1.5 Å suggests that the O-O bond in the oxygen molecule was maintained even after the discharging process. Moreover since the electrode was just rinsed and dried at 80 °C in vacuum, it is difficult to expect the formation of the lithium peroxide during the sample preparation process. Therefore the reaction mechanism of the aqueous $\text{Li}-\text{O}_2$ battery, represented by the equation (1), is highly questionable.

Fig. 2 shows a typical discharging-and charging profile of a $\text{Li}-\text{O}_2$ cell at the 1st cycle operated at 1.0 mAcm^{-2} of current density. The discharging plateau was observed at 2.8-2.9 V vs. Li, while the equilibrium potential of oxygen-water couple in the present system

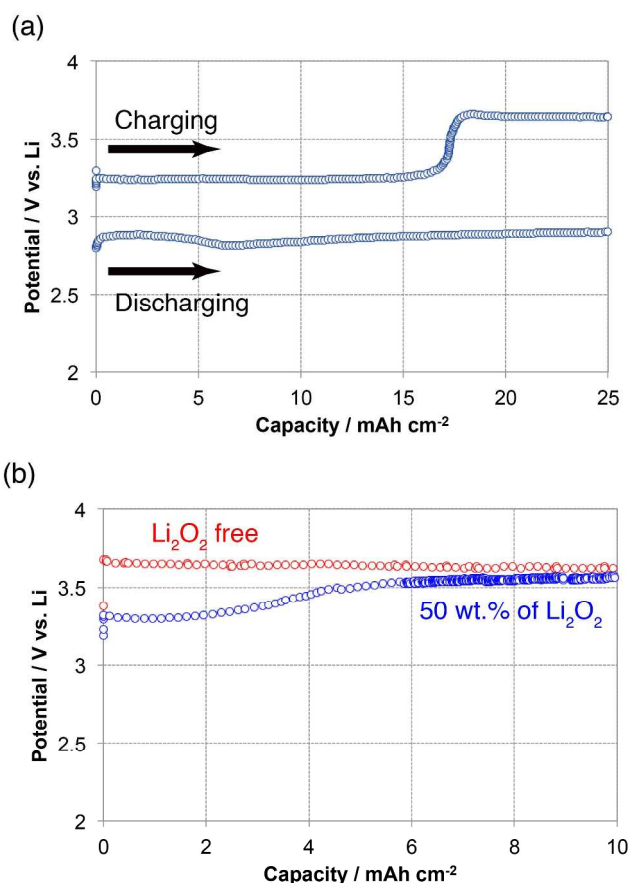


Fig. 2 Galvanostatic discharging-charging profiles of the $\text{Li}-\text{O}_2$ cell operated at 1.0 mAcm^{-2} (a) and the charging profiles of the $\text{Li}-\text{O}_2$ cells without initial discharging process, for a standard carbon-based electrode (red) and an electrode containing 50 wt% of Li_2O_2 powder (blue). The charging current density was also 1.0 mAcm^{-2} for all the electrochemical cells.

(approx. pH = 11.0) is estimated as approx. 3.6 V vs. Li according to the following Nernst equation.

$$E_{(z)}^{\circ} = 1.228 - 0.0591 \text{ pH} + 0.0147 \log \text{PO}_2$$

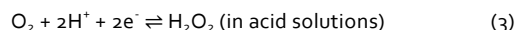
The open circuit potential: 3.1 V vs. Li, is also still lower than the equilibrium potential of the oxygen-water couple, hence the actual oxygen reduction process of the present system should be corresponding to other redox couple.

The charging profile in Fig. 2 (a) has two plateaus at 3.2 V vs. Li and 3.6 V vs. Li, while the discharging profile has only one plateau. It shows that two different reactions took place during the charging process. Considering the above discussion for the discharging process, the electrochemical reaction of the 1st plateau should be assigned to the reverse reaction of the discharging process, while the 2nd plateau represents another reaction.

In order to confirm the oxidation processes of the each plateau, the other charging tests were carried out, using a gas-diffusion electrode with / without commercial Li_2O_2 as shown in Fig. 2 (b). The electrode with Li_2O_2 also showed two plateaus while the lithium peroxide-free electrode showed only one plateau at 3.6 V vs. Li. In addition the

electrode potential of the Li_2O_2 free electrode had a plateau at 3.6 V vs. Li, exactly same electrode potential as the second plateau of the charging curve in Fig.2 (a). Thus the electrochemical reaction corresponding to the 1st plateau should be related to the Li_2O_2 . Furthermore since the electrode potential of the 2nd plateau well matches with the equilibrium potential of the oxygen-water couple, we suspect the oxidation process of the 2nd plateau corresponds to the oxidation of the OH^- based on the oxygen-water couple.

We think the reversible electrochemical reaction corresponding to the discharging plateau and the 1st plateau in the charging profile should be based on the oxygen-peroxide redox couple. According to the thermodynamic database, the typical electrochemical reaction of the oxygen-peroxide couple in aqueous system is described in the following equations.



The Nernst equation provides the following equilibrium potentials corresponding to the equation (3) and (3)'.

$$E_{(4)}^{\circ} = 0.682 - 0.0591 \text{ pH} + 0.0295 \log \text{PO}_2 / (\text{H}_2\text{O}_2)$$

$$E_{(4)'}^{\circ} = 0.338 - 0.0295 \text{ pH} + 0.0295 \log \text{PO}_2 / (\text{HO}_2^-)$$

The above equations provide the equilibrium potential of the oxygen peroxide couple at pH 11.0 is estimated to approx. 3.1 V vs. Li. The estimated equilibrium potential well matches with the open circuit potential of the Li- O_2 cell after the discharging process. Therefore the two-electron transfer process based on the oxygen-peroxide couple is the most probable reaction in the present Li- O_2 cell, we think.

It is commonly known that the discharging reaction of aqueous Li- O_2 battery is represented by the four-electron transfer process in the equation (1)'. Actually the four-electron transfer process has two two-electron steps of oxygen reduction. The first stage is the two-electron transfer process of the oxygen-peroxide couple, and the second stage is catalytic decomposition of the peroxide species. Therefore the catalytic activity of the electrode material determines the efficiency of the reaction in the equation (1)'. However since the carbon has the poor catalytic activity of the peroxide decomposition, the O-O bond is

not ruptured during the cathodic reduction process; as a consequence either H_2O_2 or HO_2^- should be the final product of the oxygen reduction process in the present aqueous system³². Furthermore the catalyst-free carbon-based electrodes are known as a good reversible electrode for the oxygen-peroxide couple in alkaline solution³³.

In order to confirm the electrochemical activity of the peroxide species, a cyclic voltammogram using an electrolyte solution containing 0.1 wt.% of H_2O_2 , was taken and compared with the normal electrolyte solution as shown in Fig. 3. Even with lower cathodic current, the electrolyte solution containing H_2O_2 showed much higher anodic current than that of the H_2O_2 -free electrolyte solution. Furthermore the anodic current never dropped down to zero above the open circuit potential. Hence it obviously shows that the peroxide species in the electrolyte solution is the active species of the OER in the present system.

We assume the peroxide species formed by the oxygen reduction process reach to the solubility limit in the present electrolyte solution with high Li^+ concentration resulting in the formation of Li_2O_2 as described in the following equation.



To summarize the above discussions concerning the reversible electrochemical process of the present Li- O_2 cell, the actual discharging reaction should consist of 2 reaction steps. The 1st step is the two-electron transfer process of the oxygen-peroxide couple and the 2nd step is the precipitation of Li_2O_2 . The 1st step is supposed to take place at the electrode-electrolyte interphase including the three-phase boundary. The electrochemically active species are O_2 and either $\text{H}_2\text{O}_2 / \text{HO}_2^-$. On the other hand, the 2nd step should occur in the bulk electrolyte solution. The possible reaction site for the 2nd step is significantly dependent upon the concentration of the peroxide species and the Li^+ . Thus we think the preferred site for the 2nd step should be inside the porous gas-diffusion electrode.

Historically the electrochemistry of oxygen was actively studied for the fuel cell applications, hence the oxygen-peroxide couple has been considered as a useless reaction that people want to suppress, while the four-electron transfer reaction of the oxygen-water couple has been considered as the desirable reaction³⁴. Furthermore the carbon corrosion by peroxide species could be another problem for the long cycling life. However, we think the oxygen-peroxide couple also has a lot of advantages as an electrochemical reaction for the rechargeable Li- O_2 batteries, because it is highly reversible. Moreover since the excess electrolyte solution is not necessary for the present system, we also expect the oxygen-peroxide couple increase the energy density of the aqueous rechargeable Li- O_2 battery.

A cycling test was performed as a proof of concept of the rechargeable Li- O_2 cell based on the oxygen-peroxide couple, as shown in Fig. 4 (a). The cell showed a very stable cycling performance for 50 cycles at the current density of 1.0 mAcm^{-2} . Notably the charging overpotential showed extremely low value <0.1 V during the 50 cycles, proving the high reversibility of the oxygen peroxide couple. The rate capability of the Li- O_2 cell is also shown in Fig. 4 (b). The cell showed very stable charging-discharging profiles, and the overpotential is clearly dependent upon the current density. Notably the charging-overpotential is even lower than the discharging

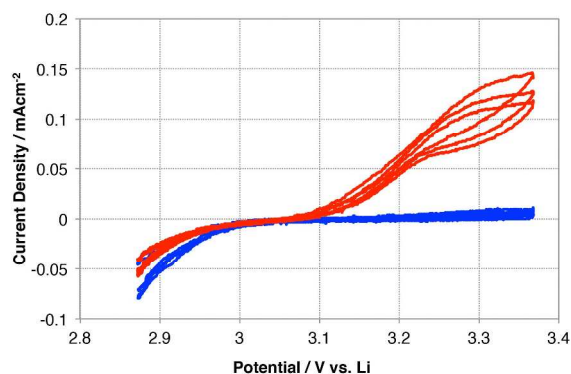


Fig. 3 Cyclic voltammograms of the Li- O_2 cell with the standard electrolyte solution (blue) and the electrolyte solution spiked with 0.1 wt% of H_2O_2 (red).

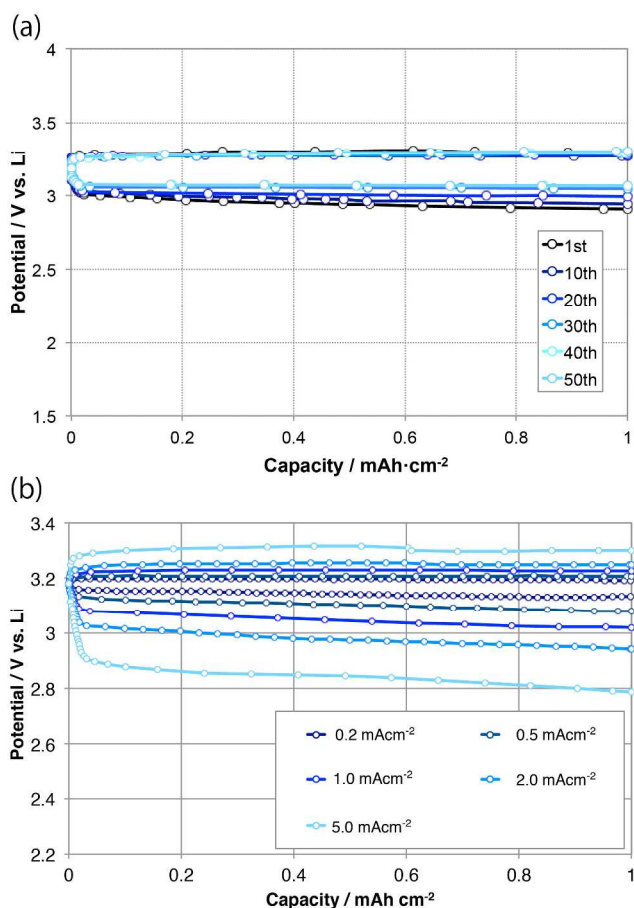


Fig. 4 A cycling performance of the Li-O₂ cell up to 50 cycles (a), and a rate capability of the present Li-O₂ cell (b). The cycling test was performed at 1.0 mA cm⁻² after an initial formation process for 50 hours.

overpotential especially at high current densities. The charging overpotential is < 0.2 V at 5.0 mAcm⁻², while the discharging overpotential is > 0.35 V. These charging-discharging results indicate that the Li-O₂ cell based on the oxygen-peroxide couple could be a high-power and a stable rechargeable battery system.

Conclusions

In this report, we investigated the reaction mechanism of the aqueous Li-O₂ cell using catalyst-free carbon-based electrode. The actual electron transfer process is based on the highly reversible oxygen-peroxide couple. The charging overpotential showed extremely low value approx. 0.1 V at 1.0 mAcm⁻² compared with typical overpotential values reported in the non-aqueous system. Therefore the novel Li-O₂ cell in this study has some possibility to make significant improvements in power density, which is the most critical challenge of the Li-O₂ batteries. Moreover the present system can minimize the water consumption problem, which is one disadvantage of the conventional aqueous Li-O₂ batteries. Therefore the oxygen-peroxide couple could be more appropriate chemistry for rechargeable aqueous Li-O₂ batteries than the oxygen-water couple, if the hydrolysis of the Li₂O₂ is completely prevented.

Our current work is focused on the electrolyte design for the stabilization of the Li₂O₂. The protected lithium metal anode is also critical to develop a practical aqueous Li-O₂ battery system.

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Notes and references

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