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Accelerated electrochemical decomposition of Li$_2$O$_2$

under X-ray illumination

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ABSTRACT: This work presents the first report detailing the effect of X-rays on the electrochemical decomposition of Li$_2$O$_2$, which is the main reaction during the charging process in a Li-O$_2$ battery. An operando synchrotron radiation powder X-ray diffraction (SR-PXD) experiment was performed. The results indicate that the electrochemical decomposition of Li$_2$O$_2$ is dramatically accelerated under X-ray irradiation. The accelerated decomposition of Li$_2$O$_2$ follows a zero-order reaction, and the decomposition rate constant is proportional to the intensity of X-ray used. A mechanism for the electrochemical decomposition of Li$_2$O$_2$ under X-ray irradiation is proposed. These results give an insight into the charging process in Li-O$_2$ batteries.

TOC GRAPHICS

KEYWORDS: Li-O$_2$ battery, synchrotron-based X-ray diffraction, fast charging, operando measurement, photoelectric effect, photoelectrochemistry, light-assisted electrochemical etching
In 1839, the photoelectric effect was first discovered by Becquerel who found that current could be generated without any external potential when AgCl was placed in an acidic solution and illuminated while connected to a Pt electrode. In the 1950’s, researchers at Bell Labs began to study the possible use of photo-electrochemical effects to convert solar energy into electric power.\(^1\) In 1972, Fujishima and Honda first reported that UV light irradiation enhanced the electrochemical decomposition of water using TiO\(_2\) as a photocatalyst.\(^2\) Their work triggered a rapid development of the photo-electrochemical cell. Many fundamental and applied advances have to day been achieved in the fields of environment and energy.\(^3\)–\(^4\) In those photo-electrochemical systems, the photoactive material as a charge carrier plays a catalytic role in the reaction, and its composition does not change after each cycle of interactions. Equally, photo energy can directly speed up the electrochemical transformation of target materials, which means the substance can be electrochemically decomposed or generated under electromagnetic irradiation. UV or visible light has shown some applications in this field.\(^5\) However, the use of X-rays as a special light source has not been reported in the electrochemical transformation of solid materials.

The electrochemical decomposition of Li\(_2\)O\(_2\) is the charging reaction in a non-aqueous Li-O\(_2\) battery, which largely influences the charging rate, overpotential and rechargeability of the system.\(^6\) Besides several issues like instability of electrolytes,\(^7\)–\(^9\) poor performance of lithium metal anode,\(^10\)–\(^11\) etc., one challenge for the Li-O\(_2\) battery is to increase the kinetics of the electrode reaction, especially for the charging process.\(^12\) Another conundrum is that the decomposition mechanism of Li\(_2\)O\(_2\) is not yet clear.\(^13\) X-ray diffraction (XRD) has been applied as a simple, useful and direct measurement to investigate the formation and decomposition of Li\(_2\)O\(_2\) for various designs of Li-O\(_2\) battery.\(^14\)–\(^18\) However, the low scattering ability of lithium and
oxygen and the limited X-ray intensity of normal in house diffractometers have led to a low sensitivity in Li$_2$O$_2$ detection. Synchrotron-based XRD offers several orders of magnitude higher X-ray intensity, much larger emitted X-ray spectrum, and a better resolution than a conventional research laboratory scale device. To the best of our knowledge, this powerful tool has been utilized only few times thus far in Li-O$_2$ battery research.$^{19-21}$

Here, we investigated the influence of X-ray irradiation on the electrochemical decomposition of Li$_2$O$_2$ in a cell with propylene carbonate (PC) electrolyte, Li and porous Li$_2$O$_2$-based electrodes. Synchrotron radiation powder X-ray diffraction (SR-PXD) was used both as a continuous X-ray source to advance the electrochemical decomposition of Li$_2$O$_2$ and an _operando_ tool to quantify the rate of Li$_2$O$_2$ decomposition. The effect of X-ray intensity on the charging process of the Li$_2$O$_2$-based cell was also investigated. This work provides a direct evidence of the acceleration of the electrochemical reactions by X-ray irradiation. In addition, fundamental information about the limiting factor and involved steps in Li$_2$O$_2$ electrochemical decomposition is revealed. Finally, to the best of our knowledge, this is the first report of X-ray irradiation being linked to effects on the electrochemical transformation of solid materials.

**Li-O$_2$ cell components**

The Li-O$_2$ cells were assembled using coffee bags with the following components: Li foil negative electrode, double-layer Solupor separator soaked in electrolyte (1 M LiPF$_6$ in PC), and porous Li$_2$O$_2$-based positive electrode. It has been reported that the intermediate superoxide species formed during the discharge reaction (Oxygen Reduction Reaction (ORR)) of a Li-O$_2$ cell results in the decomposition of PC-based electrolytes.$^8$-$^9$, $^{22-24}$ However, since i) we only tested our cells during a charging process (OER); and ii) the oxidation potential of PC is higher than that of ether electrolytes,$^9$, $^{25}$ PC electrolyte was considered suitable for this work.
The effect of X-ray irradiation on the decomposition of Li₂O₂ during the charging process of a Li-O₂ cell

![Figure 1](image1.png)

Figure 1.(a) The *operando* SR-PXD patterns of a Li₂O₂-based electrode collected every 10 min during the charging at a constant current, and (b) The SR-PXD patterns of a Li₂O₂-based electrode (I) before charging, after 3 h of charging at a constant current on a spot (II) with X-ray irradiation, and (III) without X-ray irradiation.

Fig. 1(a) shows a stacked plot of intensity vs. 2 theta collected for a Li₂O₂-based electrode under continuous X-ray irradiation during charging at a constant current of 40 mA·g⁻¹. Si (JCPDS File No: 04-014-0211) and Li₂O₂ (JCPDS File No: 04-013-3506) crystal phases were clearly observed. The absolute intensity of the Si reference peak decreased slightly as the intensity of synchrotron beam gradually faded during the measurement. However, the decrease in the intensity of the Li₂O₂ peaks is much more rapid, which confirms that the Li₂O₂ decomposition occurred during the charging process. The residual ratio of Li₂O₂ reduced to 49% after 110 minutes of charging. Qiao et al. reported that Li₂O₂ could be decomposed to Li₂O due to soft X-ray beam damage.²⁶ However, in our control experiment, while no charging current was applied to a cell containing the same amount of Li₂O₂, there is little change in the amount of Li₂O₂ under constant X-ray irradiation for 8 hours (Fig. S1 in Supporting Information (SI)).
which indicates that the Li$_2$O$_2$ degradation observed in our work cannot simply be assigned to X-ray beam damage. In addition, the Li$_2$O peaks (JCPDS File No: 00-012-0254) were not observed in any collected pattern during continuous X-ray irradiation. In order to distinguish the effect of X-ray irradiation, an identical charging experiment was performed on a matching Li$_2$O$_2$ electrode, however, in the absence of constant X-ray irradiation. In situ XRD patterns of the electrode were collected at the start and end of the charging process (Fig. S2 in SI). The result showed that in the absence of an intense X-ray irradiation, the electrochemical decomposition of Li$_2$O$_2$ ran much slower than that under the X-ray irradiation. Therefore, it can be concluded that the X-ray irradiation does accelerate the electrochemical decomposition of Li$_2$O$_2$.

To clarify this effect further, a Li$_2$O$_2$-based electrode was charged for 3 h under constant X-ray irradiation on a single spot (0.8 mm diameter). Fig. 1(b) shows the SR-PXD patterns of a Li$_2$O$_2$-based electrode before the charging, after 3 h of charging with X-ray irradiation, and without X-ray irradiation by moving the XRD measurement spot approximately 2 mm away from the irradiation spot on the same cell. Under continuous illumination, the Li$_2$O$_2$ peaks in Fig. 1(b, II) can be seen to have an obvious decrease in the intensity as compared to those peaks in the as prepared cell in Fig. 1(b, I). The residual ratio of Li$_2$O$_2$ decreased to 47% after 3 h of charging with X-ray irradiation. In contrast, the XRD pattern of Li$_2$O$_2$-based electrode after 3 h of charging without X-ray irradiation (Fig. 1(b, III)) showed only a slight reduction in Li$_2$O$_2$ peaks as compared to the as prepared cell (Fig. 1(b, I)). This corresponded to an 11% Li$_2$O$_2$ which agreed well with the calculated theoretical value (10.2%) from the charging capacity of the cell (i.e. pure electrochemical decomposition), which suggests that the Li$_2$O$_2$ decomposition is the main reaction during the charging process in our study. The results confirm that X-ray irradiation promotes the electrochemical decomposition of Li$_2$O$_2$ during the charging process of the cell.
The relationship between the X-ray intensity and the decomposition rate of Li$_2$O$_2$

![Graph](image_url)

Figure 2.(a) The curves (−) and linear curve fittings (−−) of Li$_2$O$_2$ decomposition in the electrode charged at a constant current under X-ray irradiation with different intensities (I) $I_a$, and (II) $I_b$ ($I_b=68\%$ of $I_a$), and (b) the charging curves of both cells.

In an attempt to further understand this phenomenon, the effect of X-ray intensity was examined by inserting Al filters in the path of the incident beam. From Fig. 2(a), it can be seen that after 110 min of charging, the residual ratio of Li$_2$O$_2$ reduced to 49\% with $I_a$ and 66\% with $I_b$ ($I_b=68\%$ of $I_a$), respectively, which indicates that the intensity of X-ray irradiation does influence on the rate of Li$_2$O$_2$ decomposition. The oscillating charging curves shown in Fig. 2(b) maybe caused by the influence of magnetism and/or fluctuant temperature in SR-PXD room. It is noted that no significant difference between the charging curves for both experiments are observed, and this is reasonable given that the X-ray spot only illuminated less than 0.5\% of the total area of the electrode under test. The shape of charging profile further indicates that Li$_2$O$_2$ decomposition should be the main reaction during the charging plateau, where there are few side reactions including electrolyte decomposition.$^{27}$ The XRD patterns show that there is little Li$_2$O$_2$ decomposition during the initial sloping region upon charging (about the first 10 min charging),
which might be attributed predominantly to double layer charging of the large carbon surface. Interestingly, once a steady potential of 4.2 V was established, a sluggish decomposition of Li$_2$O$_2$ during the next 20 min of charging was observed (to be discussed later), which was similar with previously published work. Generally speaking, no obvious enhancement by X-ray in the rate of Li$_2$O$_2$ decomposition was observed during the first 30 min of charging.

The X-ray intensity largely affected the electrochemical decomposition of Li$_2$O$_2$ after 30 min of charging. After 30 min, the Li$_2$O$_2$ decomposition occurs approximately linearly with respect to time (30 min $\leq t \leq 100$ min), as seen in Fig. 2(a). During this period, pseudo-zero-order kinetics was assumed to calculate the corresponding decomposition rate constant $k$:

$$W = W_0 - kt$$  \hspace{1cm} (1)

Where $W_0$ and $W$ are the original amount of Li$_2$O$_2$ before charging, and the residual amount of Li$_2$O$_2$ (g) at the charging time $t$ (min), respectively, and $k$ (g·min$^{-1}$) is the zero-order decomposition rate constant. The decomposition rate constant under the irradiation $I_b$ ($k_b = 0.4586$ g·min$^{-1}$) is 68.4% of that under the irradiation $I_a$ ($k_a = 0.6704$ g·min$^{-1}$). This ratio is almost equal to the ratio (68%) of their respective X-ray intensities ($I_a/I_b = k_a/k_b$). This means a proportional relationship exists between the X-ray intensity and the decomposition rate constant. Pure electrochemical decomposition (i.e. non-X-ray effect) in both cases made a contribution to the slight variation in this proportionality.

**The effect of the external potential on the electrochemical decomposition of Li$_2$O$_2$ under X-ray irradiation**
Figure 3. The curves (−) and linear curve fittings (−−−) of Li$_2$O$_2$ decomposition in the electrode charged at a stepwise potential of (a) 3.0 V, (b) 3.4 V, (c) 3.8 V, and (d) 4.2 V.

In order to distinguish our findings from photolysis (i.e. beam damage), the effect of the external potential on the decomposition of Li$_2$O$_2$ under X-ray irradiation was investigated by charging one cell at a stepwise potential from 3.0 V to 4.2 V for 120 min at each potential under a constant intensity of X-ray irradiation, as shown in Fig. 3. Zero-order kinetics of Li$_2$O$_2$ decomposition does also apply here when the cell was charged at constant potentials. In fact, only 0.3%, 1.2% and 2.6% of Li$_2$O$_2$ decomposed at the charge voltages of 3.0 V, 3.4 V and 3.8 V during 120 min of charging, respectively. However, when the cell was held at a potential of 4.2 V for 120 min of charging, more than 50% of Li$_2$O$_2$ was decomposed, which is 40 times faster than that charged at the same potential without X-ray irradiation (Fig. S2(b) in SI). The big difference between the decomposition rate constants at different potentials demonstrates that X-ray acceleration was observable only when a certain external potential provided, which may be attributed to some steps involved requiring a certain energy barrier. From these results, it has been well established that both X-ray and external potential play important roles in the fast electrochemical decomposition of Li$_2$O$_2$. 
Figure 4. Scheme illustrating the electrochemical decomposition of Li$_2$O$_2$ under the X-ray irradiation.

Based on our observations, a possible process to describe the X-ray accelerated, electrochemical decomposition is proposed by the following equations:

$$\text{Li}_2\text{O}_2 \xrightarrow{\text{X-ray}} [\text{Li}_2\text{O}_2]^{x^+} + xe^-$$  \hspace{1cm} (2)

$$[\text{Li}_2\text{O}_2]^{x^+} \xrightarrow{\text{external potential}} \text{Li}_{2-x}\text{O}_2^{x^+} + x\text{Li}^+$$  \hspace{1cm} (3)

$$\text{Li}_{2-x}\text{O}_2^{x^+} \xrightarrow{\text{external potential}} (2-x)\text{Li}^+ + \text{O}_2 \uparrow + (2-x) e^-$$  \hspace{1cm} (4)

In the first step, the X-rays eject photo electrons from the Li$_2$O$_2$ crystals to form a partly positive species, [Li$_2$O$_2$]$^{x^+}$. From the experimental results, the higher intensity of X-ray can produce more [Li$_2$O$_2$]$^{x^+}$, resulting in a faster decomposition. Therefore, this step can be considered as a kinetically limiting step. Note that the external potential here is also important for driving these free electrons to the counter electrode. Without the external potential, these electrons can recombine quickly with [Li$_2$O$_2$]$^{x^+}$. Ma et al. revealed that X-ray illumination can eject the electrons from a substance, but it cannot complete the electrochemical process.$^{28}$ In order to keep electric neutrality, [Li$_2$O$_2$]$^{x^+}$ can lose some Li$^+$ and transform into Li$_2$O$_2$ with some Li vacancies.
(Li$_{2-x}$O$_2$*) in the second step. Ong et al. demonstrated that the formation energies of a Li vacancy in an intralayer and interlayer of Li$_2$O$_2$ are 3.8 eV and 4.1 eV, respectively. In other words, a certain driving force is required for the formation of Li$_{2-x}$O$_2$*, which is in agreement with our results. The moveable Li vacancy can pin into Fermi level at the top of anti-bonding peroxide $\pi^*(2p_x)$ and $\pi^*(2p_y)$ levels in the valance band, leading to an enhanced electronic conductivity of Li$_{2-x}$O$_2$*, which will promote the Li$_{2-x}$O$_2$* decomposition, especially at a high rate of charging. During this step, surface Li$^+$ can be preferentially released from [Li$_2$O$_2$]$^{x+}$ into the electrolyte to form Li$_{2-x}$O$_2$* with surface Li vacancies. Then, the inner Li atoms can diffuse to the surface Li vacancies, since the diffusion energy is low about 0.36 eV. In the last step, the crystal structure of Li$_{2-x}$O$_2$* completely collapses to yield Li$^+$ and O$_2$. The energy for the decomposition of Li$_{2-x}$O$_2$* and release of O$_2$ is provided by the external potential during this step. From the beginning of the reaction, the amount of the intermediates ([Li$_2$O$_2$]$^{x+}$ and Li$_{2-x}$O$_2$*) gradually increase, and it might take some time to achieve the steady-states of these intermediates before a breakdown of Li$_2$O$_2$ framework, which could explain the sluggish decomposition of Li$_2$O$_2$ at the early stage. It can be deduced that the external potential contributes to all three steps involved, and a potential threshold might exist in the second and/or last step. In summary, X-ray increases the kinetics of the rate-determining reaction (the first step), while the external potential meets the thermodynamics requirements in the second and/or last steps. The mechanism of X-ray acceleration effect on the Li$_2$O$_2$ electrochemical decomposition is proposed by the scheme in Fig. 4.

Finally, this process can be considered similar to light induced electrochemical etching and lithography. However, the resolution of these techniques is limited by the wavelength of light source used (normally, UV or visible light). Therefore, it can be expected that X-ray induced
electrochemical etching and lithography would achieve a considerably higher resolution, which could make a significant contribution in the microelectronic industry.\textsuperscript{35}

In summary, for the first time, the accelerating effect of X-rays on the electrochemical decomposition of Li\textsubscript{2}O\textsubscript{2} was explored by \textit{operando} SR-PXD. An X-ray acceleration mechanism was proposed based on the experimental results. The conclusion obtained is: (i) X-ray, as a photo energy, accelerates the electrochemical decomposition of Li\textsubscript{2}O\textsubscript{2}; (ii) the electrochemical decomposition of Li\textsubscript{2}O\textsubscript{2} under X-ray irradiation follows a zero-order reaction during the main period; (iii) the rate of Li\textsubscript{2}O\textsubscript{2} decomposition is proportional to the intensity of X-ray used; (iv) the electrochemical decomposition of Li\textsubscript{2}O\textsubscript{2} under X-ray irradiation may involve a three-step reaction with [Li\textsubscript{2}O\textsubscript{2}]\textsuperscript{x+} and Li\textsubscript{2-x}O\textsubscript{2}\textsuperscript{*} as intermediates; and (v) The X-ray interaction promotes kinetics, while the external potential overcomes the thermodynamic barriers. The findings here indicate that there could be other routes than a single-step reaction for Li\textsubscript{2}O\textsubscript{2} electrochemical decomposition in Li-O\textsubscript{2} battery. If some way (e.g. by electrocatalysts) to induce the ionization of Li\textsubscript{2}O\textsubscript{2} and/or enhance its conductivity could be adopted, an accelerated charging process can be expected, and the selectivity will be consequently improved due to the overwhelming kinetics of the main reaction, Li\textsubscript{2}O\textsubscript{2} decomposition. High-resolution electrochemical etching could be achieved with the assistance of X-ray irradiation, and the etching speed could be tuned by X-ray intensity. This advance could be applied in the microelectronics industry.

\textbf{Experimental Methods}

\textbf{a. Li\textsubscript{2}O\textsubscript{2}-based electrode preparation and the electrochemical cell assembly.} The porous Li\textsubscript{2}O\textsubscript{2}-based positive electrodes consisted of Super P carbon (lithium battery grade, ErachemComilog), Kynar 2801 (a copolymer based on PVDF, Arkema), Li\textsubscript{2}O\textsubscript{2} powder (technical grade, 90\%, Sigma-Aldrich) and silicon (99.5\%, Alfa Aesar) in weight ratio of
Silicon was added as an inert internal reference to calculate the amount of Li$_2$O$_2$ present in a given sample, since it provides stable and strong diffraction peaks in the XRD patterns. Super P carbon, Li$_2$O$_2$ and silicon were mixed by high energy ball-milling in a coffee bag for 1 h. To the mixture, Kynar binder and acetone ($\geq 99.0\%$, Fluka) were added to prepare a slurry, which was hand-milled for 30 min. The slurries were cast drop wise onto an aluminum mesh with a diameter of 1.3 cm and a flat area of 1.32 cm$^2$. The acetone was then left to evaporate, and the electrodes were further dried at 120 °C for 5 h in a vacuum (Buchi Glass Oven B-585). All the operations were performed in an Ar-filled glove box (H$_2$O and O$_2$< 1 ppm). The electrode construction is similar with that of a cathode in a Li-O$_2$ cell.$^{36}$

All the electrochemical cells were assembled in an Ar-filled glove box using a pouch cell (i.e. “coffee bag” cell) with the following components: Li foil negative electrode, double-layer Solupor separator soaked in electrolyte (1 M LiPF$_6$ in PC, Ferro, Purolute), and porous Li$_2$O$_2$-based positive electrode described above (Fig. S3(a) in SI).

b. Operando SR-PXD measurement. Operando SR-PXD (measuring the synchrotron-based XRD during the charging process of a cell) was conducted using beamline I711 at the MAX II synchrotron of Max IV Laboratory in Lund, Sweden (Figs. S3(b-d) in SI).$^{37}$ The cells were mounted in transmission mode, and an Oxford diffraction Titan CCD was used to collect diffraction pattern. Lanthanum hexaoride (LaB$_6$, SRM-660) was used as a reference material to calibrate the different parameters of powder diffraction instrument (wavelength, sample-to-detector distance and tilt angle). The refined X-ray wavelength was 0.991 Å. During a standard experiment, the frames were collected under continuous X-ray irradiation (an exposure time of 20 s was used to collect a single frame, followed by a 5 s dark period during the detector read out). A frame is the integrated data collected on the detector during the exposure. This data was
later converted to an intensity vs. 2 theta plot, through circular integration. The diameter of X-ray irradiation spot was about 0.8 mm. To adjust the X-ray intensity, Al filters were employed. Initially, a few frames were collected in the absence of any charging current. This was then followed by the collection of further frames in an operando mode, i.e. during charging the cells using an external potentiostat (SP-240, Bio-Logic SAS) at a constant current of 40 mA·g$^{-1}$ from open circuit voltage (OCV) to 4.5 V. Data were also collected while one cell was charged under stepwise potentiostatic control from 3.0 V to 4.2 V for periods of 120 min at each potential under the X-ray irradiation with the constant intensity. The program Fit2D was used to integrate the 2D diffraction images,$^{38}$ and the FullProf program was employed to refine the XRD patterns and analyze the weight fraction of Li$_2$O$_2$ and Si.$^{39}$ The residual ratio of Li$_2$O$_2$ in each cell during the charging process was calculated from eq. S1 in SI.

c. **In house in situ X-ray diffraction measurement.** In order to study the electrochemical decomposition of Li$_2$O$_2$ without the influence of X-ray irradiation, in house in situ XRD analysis (XRD measurement of the whole cell without unpacking it before and after the charging process) was also performed in transmission mode using a STOE diffractometer with a position-sensitive detector and Co Kα radiation ($\lambda = 1.789$ Å), operating at 45 kV and 32 mA. The residual ratio of Li$_2$O$_2$ in each cell charged at a constant current or constant potential was calculated, based on eq. S1 in SI as well.

**ASSOCIATION CONTENT**

Supporting Information. The curve of Li$_2$O$_2$ decomposition in the electrode with the same amount of Li$_2$O$_2$ where no charging current was applied under constant X-ray irradiation for 8 h, *in situ* XRD patterns of a Li$_2$O$_2$-based electrode before charging and after 10 h charging, images
of a cell sealed in a coffee bag and SR-XRD, schematic diagram of the beamline I711, and the formula for calculating the residual ration of Li$_2$O$_2$ in each cell during charging process. This material is available free of charge via the Internet at http://pubs.acs.org.

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**Notes**

The authors declare no competing financial interests.

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**REFERENCES**


