Topical Review

Review of the structure and performance of through-holed anodes and cathodes prepared with a picosecond pulsed laser for lithium-ion batteries

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Abstract
To move the performance of lithium-ion batteries into the next stage, the modification of the structure of cells is the only choice except for the development of materials exhibiting higher performance. In this review paper, the employment of through-holing structures of anodes and cathodes prepared with a picosecond pulsed laser has been proposed. The laser system and the structure for improving the battery performance were introduced. The performance of laminated cells constructed with through-holed anodes and cathodes was reviewed from the viewpoints of the improvement of high-rate performance and energy density, removal of unbalanced capacities on both sides of the current collector, even greater high-rate performance by hybridizing cathode materials and removal of irreversible capacity. In conclusion, the points that should be examined and the problem for the through-holed structure to be in practical use are summarized.

Keywords: lithium-ion battery, picosecond pulsed laser, through-holed structure, high-rate performance, energy density, prelithiation

1. Introduction
Lithium-ion batteries (LIBs) have increased the convenience of our daily lives as power sources for mobile devices [1, 2]

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and have established the world of electrically powered vehicles [3, 4]. LIBs are chemical devices in which chemical energy is converted to electrical energy in the discharging process and electrical energy is converted to chemical energy in the charging process [5, 6]. Chemical reactions provide the energy conversion in LIBs. Chemicals contained in the anode, cathode, electrolyte, solvent, binder, and conductive additives have been designed not only to exhibit the maximum performance but also not interact unfavorably with other chemicals [7–9]. Usually, the electrolytes, solvents, binders, conductive additives and so on have also been modified for anode and
cathode materials to exhibit the maximum performance \cite{10,11}. Moreover, it is thought that improvements in LIB performance by developing new materials are presently stagnant, although solid electrolytes will improve LIB performance in the future. The development speed of new LIBs cannot meet the rate of our increasing demands. Recently, many reports showing that LIB performance can be improved by optimizing the cell structure have been published \cite{12–15}. Although optimization of the individual parts in LIBs, such as the anode, cathode and separator, leads to only a small improvement, the sum of the optimization of all parts in LIBs will realize a large improvement. As the reader can understand, the performance of present LIBs is much higher than the LIBs that were initially developed and commercialized. However, it should be noted that the anode and cathode materials in current LIBs remain almost unchanged from early types of LIBs. Even at the present time, various optimizations of LIB structures to achieve higher performance than one of the present LIBs have been attempted \cite{16–19}. However, an essential problem is how to optimize the structure of each part in LIBs, as prepared in the mass-production process of LIBs, without complicating the production process and increasing the production cost of LIBs. In other words, although many researchers have developed good ideas for improving battery performance \cite{16}, they lack sufficient technological capability to materialize those ideas without complications. Thus these ideas will be of little practical use to high-performance LIBs.

We developed a practical system to prepare through-holes on anodes and cathodes with a laser system. The formation of through-holes on anodes and cathodes can improve the high rate and energy density performance of LIBs. This laser system can be introduced to the present mass-production lines of LIBs without any change in the LIB production line (figure 1).

In the production of roll-to-roll lines of anodes and cathodes, anode and cathode layers are formed by casting anode and cathode slurries on copper (Cu) and aluminum (Al) current collector foils. After drying, the surfaces of the dried anodes and cathodes are irradiated with the laser beams of the picosecond pulsed laser. During the irradiation by the laser beams, something is scattered by the impact of the laser beam. As a result, fumes of materials of the current collector, anode and cathode materials, which are formed by vaporization, flutter around the spots of the laser beams. The scattered material and fumes have a negative influence on the performance and safety of LIBs. Thus, to collect these materials, we developed a custom-designed dust catcher, which is placed around the beam spots. In addition, a foreign matter detector on the anode and cathode surfaces is placed after the dust catcher to reconfirm that adhesion of foreign matter does not occur on the laser-treated anode and cathode surfaces. The laser system, dust catcher and foreign matter detector are absolutely necessary in our system so that the performance and safety of the LIBs prepared with the systems are maintained.

During the mass production of LIBs, laser technologies that are also central to this study are used in the steps of cutting electrode sheets, welding conductor tabs to conductor lugs of the anodes and cathodes and sealing packages of LIBs \cite{20–22}. Laser technologies are widely used in the present mass production of LIBs. These laser technologies are quite safe and can reduce the cost of the LIB fabrication process. In addition, as reviewed in this paper, many papers on the modification of anode and cathode structures with laser technology have already been published \cite{15,23–27}. The structures of anodes and cathodes, which were prepared and discussed in the papers \cite{23–26}, are summarized in figure 2. Each Li$^+$ transfer in the structures is explained with the
schematic description. The structures shorten the distance to the particle surface of anodes and cathodes for Li$^+$ ion transfer in anode and cathode layers and produce the open spaces for the volume expansion during anode charging processes. Ultraviolet [22, 23, 25], infrared [15, 24] and visible light [26] laser beams are used to irradiate the anode and cathode surfaces with a repetition rate of 1–500 kHz and laser pulse lengths of 4–200 ns and 190 fs, respectively [15, 23–26]. Pfleging wrote an interesting review paper on laser electrode processing [14].

Based on the concept for enhancing Li$^+$ ion transfer [14, 27], we also modified the anode and cathode surfaces with laser beams [28]. The difference between our study and other studies is that in our research, we drill through-holes in the anodes and cathode with the laser beams, while in other studies, only line and grid structures with various widths and periods are formed on the anode and cathode surfaces without through-holing the current collectors. The employment of through-holed anodes and cathodes will contribute to maintaining the battery performance and safety of LIBs because
Li$^+$ ions in a cell contribute to intercalation/de-intercalation into/from all anodes and cathodes through the through-holes (figure 3).

The through-holing of anodes and cathodes supplies various other advantages to LIBs, largely improves the performance of LIBs, and suppresses the deterioration of the performance. We demonstrated the improvement and maintenance of LIB performance by through-holing. In this review paper, the characterization and performance of through-holed anodes and cathodes prepared with a picosecond pulsed laser are introduced. The points that are reviewed in each chapter are the characterization of through-holes, improvement of high-rate performance, discussion of the reason for the improvement of high-rate performance, energy density with through-holed cathodes, the greater improvement in high-rate performance with a through-holed lithium iron phosphate (LiFePO$_4$, LFP)/activated carbon (AC) hybrid cathode and the improvement of the energy density of anodes by removing irreversible anode capacity with lithium predoping. Readers can be persuaded by the results reviewed that the laser technology we have developed can be of practical use in high-performance LIBs.

2. Preparation of through-holed anodes and cathodes

We developed two types of laser systems, one for lab experiments and another for the mass production of LIBs. In this paper, the laser system for lab experiments is described. The laser system for the mass production can produce one through-hole by one laser shot and therefore the speed of the through-hole production is 100 000 hole s$^{-1}$. In the lab system, the laser system is constructed with a picosecond pulsed laser (the laser device is an RGH-532-8, Rayture Systems Co., Ltd), scanner system (RAYLASE Supersvan III) and telecentric $F_{\theta}$ lens (SILL Optics S4LFT3161/292), as shown in figure 4 [28]. The laser system was set at wavelengths, pulse lengths and laser repetition rates of 532 nm, <20 ps and 100 kHz, respectively. The average power and pulse energy that were measured on the anode and cathode surfaces were 2 W and 20 $\mu$J, respectively. The beam propagation ratio, $M^2$, was $\leq 1.3$, the focus diameter was approximately 20 $\mu$m, and the focal length of the optics used was 163.9 mm. Holes of 20 $\mu$m diameter were formed in the graphite anode and LFP cathodes. A laser pulse of 300 shots was induced in the anode and cathode surfaces to form a through-hole. The drilling rate in this process was 4.2 ms/hole at 20 $\mu$J and 100 kHz.

3. Characterization of the through-holed anodes and cathodes

3.1. Structural analysis of through-holes and active material layers

Figure 5 shows scanning electron microscopy (SEM) images of the LFP cathode and graphite anode surfaces shot by the laser pulse 5–300 times. In the case of both the graphite anode and LFP cathode, as the number of laser shots increased, the anode and cathode materials were hollowed, and larger craters with large cone angles formed on the surfaces of the incident laser side of the anodes and cathodes. The relationship between the number of laser shots and the size of the crater is different between the graphite anode and LFP cathode layers. The depth and diameter of craters produced by laser impacts on the LFP cathode layer are larger than those on the graphite anode layer. The dependence of the degree of damage of the anode and cathode layers by laser impacts on the materials of the anode and cathode is currently under consideration. From the SEM images of the laser emission side, laser shots of 50- to 70-fold can form through-holes both on the graphite anode and LFP cathode. The holes formed on the laser emission side have a smaller cone angle than one of the holes formed on the
laser incident side. The targeted hole diameter and opening rate of the graphite anode and LFP cathode were 20 µm and 1%, respectively, in this case. The opening rate ($R_{\text{opening}}$) of holes formed on anode and cathode layers is defined as the percentage of the holed area per the layer surface area, which is calculated by equation (1)

$$R_{\text{opening}}(\%) = \frac{A_{\text{hole}}}{A_{\text{unit part}}} \times 100. \quad (1)$$

In which $A_{\text{hole}}$ and $A_{\text{unit part}}$ are the areas of a hole and a unit part of a grid-patterned anode and cathode, respectively [29]. Based on the SEM images of the through-holed graphite anode and LFP cathode, the average diameter and opening rate calculated with the average diameter of the through-holed graphite anode and LFP cathode examined in this study are 19.5 and 20.1 µm and 1.21% and 1.04% for the graphite anode and LFP cathode, respectively. In the experiments with the targeted hole diameter and opening rate of 20 µm and 1%, the prepared graphite anode and LFP cathode showed a loss of 2%–3% of the weight of the anode and 5%–8% of the weight of the cathode, when compared with the as-prepared anode and cathode before the laser irradiation experiments.

Figure 6 shows the cross-sectional SEM images of the through-holed graphite anode and LFP cathode [30]. It can be confirmed from the SEM images that the through-holes formed on the anode and cathode have a tapered shape, as mentioned above. The hole sizes characterized by the cross-sectional area passed over by Li$^+$ ions were defined as the hole diameter at the current collector of the laser emission side. The atomic distribution in the prepared through-holes was analyzed with SEM-energy dispersive x-ray (EDX) spectroscopy to confirm where the elements in the LFP cathode material and Al current collector had gone after through-holing with the laser beam (figure 7) [31]. From the SEM-EDX results, the elemental Al that evaporated with the heat of the laser beam was dispersed and deposited as a solid metal on the laser-incident side of the sidewall of the through-holes formed after laser treatment of the LFP cathode. When the laser beam is drilling through the Al current collector, the Al current collector is heated by the absorbed laser energy. The Al evaporates and

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**Figure 4.** A schematic description of the preparation system of the porous electrodes with a picosecond pulsed laser and a galvanometer scanner system. Reprinted from [28], Copyright (2018), with permission from Elsevier.
Figure 5. Field emission-scanning electron microscopy (FE-SEM) images of the LFP cathode and graphite anode surfaces shot by the picosecond pulsed laser 5–300 times.

Figure 6. Cross-sectional SEM images of the prepared (a) through-holed graphite anode and (b) LFP cathode. The average hole size on the laser emission side was a constant 20 µm in all SEM images. Reproduced from [30]. © IOP Publishing Ltd. All rights reserved.

is then deposited on the sidewall of the holes. The impact of laser incidence on the anode and cathode layers induces the growth of voids produced in the anode and cathode layers. The focused ion beam (FIB)-SEM image (b), which was obtained at the sidewall of the through-hole, shows an increase in the number and size of voids in the LFP layer after laser treatment when compared with one (a) before laser treatment (figure 8) [31]. The increase in the number and size of the voids causes a decrease in the electrical conductivity of the anode and cathode layers and an increase in the accessibility of Li\textsuperscript{+} ions to the anode and cathode material surfaces, resulting in an improvement in the charging/discharging high-rate performance. The decrease in the electrical conductivity of the LFP layer around the through-holes was confirmed by measuring conductive current images with atomic force microscopy [31]. As mentioned in the next section, the through-holed anode and cathode exhibited large improvements in high-rate performance. The main reason for the improvement is the additional occurrence of the insertion and disinsertion of Li\textsuperscript{+} ions to/from the LFP layer from/to the sidewalls.
of the through-holes in the discharging/charging processes, although the insertion and disinsertion of Li\(^+\) ions to/from the anode and cathode layers occur only at the surface of the anode and cathode layers. The formation of micrometer-sized voids via laser treatment becomes the second factor for improving the high-rate performance. That is, the Li\(^+\) ions can diffuse much faster through the micrometer-sized voids produced by the laser treatment in the anode and cathode layers than the diffusion of Li\(^+\) ions in the anode and cathode layers without the micrometer-sized voids. On the other hand, although the formation of through-holes increases the accessibility of Li\(^+\) ions to/from anode and cathode layers and material particle surfaces, the through-hole formation contributes negatively to the anode and cathode performance via the decrease in the electrical conductivity of the anode and cathode layers. As a result of the subtraction of positive and negative factors, the through-holed anode and cathode exhibited an overall improvement in the high-rate performance. The three-dimensional diffusion of Li\(^+\) ions in the active layers of the anode and cathode modified by laser technology has recently been reported and discussed [32, 33]. In the anodes and cathodes having the through-holes, not only does the three-dimensional diffusion of Li\(^+\) ions occur in the active layer formed on the one-side of a current collector but
also larger three-dimensional diffusion of Li\(^{+}\) ions occurs in the active layer and between the active layers on both sides of a current collector. The comparison between the experimental and simulation results will suggest the mechanism of the improvement and will indicate the most suitable diameter of holes formed, the percentage of holed areas (i.e. opening rate) and the arrangement of holes on the anode and cathode layers. Further examination and discussion are needed and work along this line is currently in progress.

### 3.2. Chemical analysis of active materials in anode and cathode layers after laser treatment

To chemically analyze the anode and cathode materials that were exposed to laser irradiation, the chemical states of the anode and cathode materials were determined by Raman spectroscopy and x-ray photoelectron spectroscopy (XPS). The G-, D- and 2D bands of graphite (b) before and (a) after laser treatment of graphite anodes and (c) graphite powder before preparation of the graphite anode were compared (figure 9) [34]. In the through-holed graphite anode, the hole diameter was not 20 \(\mu\)m, which was mentioned above, but rather 50 \(\mu\)m because a larger area in the edge part of a through-hole formed by the laser beam can be analyzed with a laser Raman microscopy system (the Raman laser beam diameter is 50 \(\mu\)m). The G-band appearing at approximately 1590 cm\(^{-1}\) is an in-plane vibrational mode involving the sp\(^2\) hybridized carbon atoms that compose the graphene sheet, and the G-band position is highly sensitive to the number of graphene layers present in the sample. The position and peak shape of the D- and 2D-bands indicate the difference in the degree of the defect of the edge area of graphene layers [35]. The comparison of the G-, D- and 2D bands before and after laser treatment can be used to evaluate the change in the chemical state of graphite. The spectra (a)–(c) showed the same ratio of G/D peak intensities, indicating that the chemical state of graphite materials located around the edge of the through-hole is not different from that of graphite, which forms an anode layer and is in powder form. In addition, after the laser treatment, the through-holed anode did not show a new Raman peak. The chemical state of carbon 1s in graphite deposited in the through-holed and nonholed layers was then measured with XPS (figure 10) [34]. In the case of both through-holed and nonholed graphite layers, the main peaks can be thought to be from C–C and C=O bonds [36]. The ratio of the peak areas of C–C and C=O bonds did not change before and after the laser treatment. The new XPS peak did not appear after the laser treatment. In summary, it was concluded that graphite was not damaged by the irradiation of the laser beam and that the laser beam only blows off the anode materials located in the laser spots.

The cross-section of the LFP cathode was analyzed with microscopic Raman spectroscopy. Figure 11 shows Raman mapping of the cross-section of a through-hole of the LFP cathode to show the distribution of chemicals around the through-hole [31]. Based on the Raman spectrum at the microscopic points over the sample, the distribution of LFP, carbon black used as conductive additive and Fe\(_2\)O\(_3\), was formed by the oxidation of LFP, was classified by colors of blue, black and red. The formation of Fe\(_2\)O\(_3\) around the through-holes can be observed, and on the other hand, the cross-section of the nonholed LFP cathode in the Raman mapping did not show the existence in the LFP layer, although the data are not shown here. The irradiation of the LFP layers with the laser beam causes little change in the chemical state. As mentioned later, the loss of the capacity of LFP of approximately 5% can be thought to be from the change of LFP to Fe\(_2\)O\(_3\). The same experiment was applied to the LiNi\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)O\(_2\) cathode material, and the LiNi\(_{1/3}\)Mn\(_{1/3}\)Co\(_{1/3}\)O\(_2\) was not damaged by the laser beam. It was expected that the degree of damage caused by the laser beam would be different on these materials.

### 4. Improvement of the high-rate performance and energy density of cathodes and anodes

The prepared through-holed graphite anode and LFP cathode were examined in high-rate performance tests at C-rates of 0.1, 0.5, 1, 2, 5 and 10 C. Figure 12(a) shows the discharge curves observed with the (I) graphite anode and (II) LFP cathode at

![Figure 9. Raman spectra of (a) graphite near the hole on the through-holed graphite anode (opening rate of hole on the anode: 1%, hole size: 50 \(\mu\)m), (b) graphite anode deposited on the Cu current collector without holes and (c) graphite powder. Reproduced with permission from [34].](image-url)
Figure 10. C 1s XPS spectra in (a) graphite layer having the through-holes (opening rate of hole on the graphite anode: 1%, hole size: 50 µm) and (b) nonholed graphite layer formed on the Cu current collector. Reproduced with permission from [34].

Figure 11. (a) Microscope and (b) Raman mapping images of a through-holed LFP cathode with an opening rate of 1% and a hole diameter of 20 µm. Reproduced with permission from [31].
Figure 12. (A) Discharge curves of (I) the through-holed graphite anode (hole diameter: 20 µm, hole opening rate: 1%) and (II) the porous LiFePO$_4$ cathode (hole diameter: 20 µm, hole opening rate: 1%) observed at C-rates of (a) 0.1, (b) 0.5, (c) 1, (d) 2, (e) 5 and (f) 10 C. (B) Discharge capacity retention vs C-rate in (I) graphite anodes and (II) LiFePO$_4$ cathodes. Nonholed (◦) and through-holed (●) anodes and cathodes, hole diameter: 20 µm, hole opening rate: 1%. Reproduced from [30]. © IOP Publishing Ltd. All rights reserved.

different C rates. The discharge curves observed at different C-rates exhibit normal curves that have a decreasing average discharge voltage trend with increasing C-rate. Figure 12(b) shows the discharge rate performance of the through-holed and nonholed (I) graphite anode and (II) LFP cathode at room temperature. All the cells tested were charged with a 0.1 C to ensure identical initial conditions for each discharge. It is clear from this figure that the discharge rate performance of both the graphite anode and LFP cathode is influenced by the through-holes on the anode and cathode. In the nonholed anode and cathode, the capacity retention is 88% and 29% at 10 C for the graphite anode and LFP cathode, respectively. On the other hand, the through-holed graphite anode and LFP cathode exhibit capacity retentions of 93% and 68%, respectively, at 10 C. Notably, the difference in capacity retention between the through-holed and nonholed anode and cathode increases with increasing C rate. The trend indicates that the accessibility of Li$^+$ ions from/to the graphite and LFP particle surfaces for the lithiation/delithiation processes is enhanced by through-holing of the anodes and cathodes. Additionally, in the case of laminated cells of through-holed graphite anodes and cathodes, the advantage of through-holing of the anode and cathode could be confirmed (figure 13) [28]. NMC333 and NCA cathode materials were also tested for the through-holed structure prepared with the picosecond pulsed laser. Although the results are our unpublished data, Li(Ni$_{1/3}$Mn$_{1/3}$Co$_{1/3}$) (NMC333) showed the behavior similar as the LFP cathodes and however, LiNi$_{a}$Co$_{b}$Al$_{1-a-b}$O$_{2}$ ($a > 0.85$, NCA) exhibited large decrease in the capacity. The reason for the degradation of the capacity of the NCA cathode might be heat damage caused
by the laser irradiation because the NCA used is weak to heat [37].

The through-holing structures lead to exposure of anode surface area to electrolyte and enhance the formation of unstable electrode solid electrolyte interphase (SEI) film. Based on the through-holing structures of anodes, the surface area of anode surfaces was calculated. The summary of the calculation results is shown in supporting information of [38]. The relative percentages of the total surface area of the through-holed graphite/graphite cathodes to one of the non-holed graphite/graphite electrode was 106%. The increase in the surface area will cause the observation of the increase in larger irreversible capacity. However, larger increase in the irreversible capacity could not be observed in the through-holed graphite anodes [38]. The results are unexpected. Therefore, the irreversible capacity and charging/discharging cycle stability should be examined later carefully.

In the present LIBs, anode and cathode material layers have become as thin as possible to realize shorter charging time and high current output, namely, high-rate performance of cells. However, the employment of an anode and cathode composed of thin layers brings about a decrease in the volumetric energy density of a LIB cell because the number of current collectors and separators in a cell cannot accept any increased electrical energy during charging. Put another way, if thicker anode and cathode layers can be used in LIBs, the energy density of LIBs will be improved. The through-holed anode and cathode exhibiting high-rate performance can improve the energy density of a cell based on this point.

Figure 14 shows discharge capacity retention vs C-rate for nonholed (A), through-holed (B) and nonthrough-holed (C) LFP cathodes. The thicknesses of the LFP layer are 15.0 (●), 26.1 (●) and 43.0 (●) µm. Reprinted from [38], Copyright (2019), with permission from Elsevier.
performance degrades to a large degree. This effect can usually be observed in the nonholed LFP cathodes. The through-holed and nonthrough-holed LFP cathodes did not exhibit this dependency of high-rate performance on layer thickness. Therefore, the results demonstrate that LFP cathodes with a thicker layer can maintain the discharging capacity even at a high C-rate and that a thicker cathode with a through-holed structure can be applied to present LIBs to increase the energy density.

5. Improved high-rate discharging performance of ‘unbalanced’ LFP cathodes with different LFP loadings

As mentioned above, the improvement of high-rate performance can be given to the anodes and cathodes by the holing of anode and cathode layers if the holes are not through-holes because of the additional occurrence of the insertion and disinsertion of Li$^{+}$ ions to/from the LFP layer from/to the sidewalls of the through-holes in the discharging/charging processes. Through-holing can provide additional performance to anodes and cathodes. One of the additional performances is the effect of cancelling the imbalance in capacity between active layers formed on both sides of a current collector. The imbalance in capacity between the active layers formed on both sides of a current collector foil prohibits full discharge at a high C-rate. The prohibition of full discharge due to this imbalance in capacity cannot usually be recognized because the active layers formed on both sides of current collectors are formed with strictly identical amounts of the active materials to make the capacity equal on both sides of a current collector in the commercially available products of LIBs. However, the imbalance in the capacity on both sides of anodes and cathodes occurs occasionally, such as the falling of active materials from anodes and cathodes.
and deactivation of materials during the operation and storage of LIBs. To make effective use of LIBs over the long term, cancellation of the capacity imbalance should be given to the present LIBs. The through-holing structure of anodes and cathodes can produce this cancellation effect in the cell of an LIB. The capacity-imbalanced cathodes were prepared in a systematic order, as shown in the table of figure 15 [39]. The rate performance tests of the cathodes with different degrees of imbalance were performed at 25 °C. Figure 15(b) shows the results obtained with nonholed LFP cathodes having a different degree of capacity imbalance of the LFP layers formed on both sides [39]. The percentages of the theoretical capacity of the cathode that can be discharged at a high C-rate considering the loading amounts of active materials loaded on current collectors decreases with an increase in the degree of the capacity imbalance, especially under this experimental condition. When the degree of imbalance is higher, the total amounts of active materials loaded to a current collector, that is, the total capacity, are lower. Therefore, unbalanced cathodes should exhibit higher rate performance. However, due to the capacity imbalance fixed on both sides of a current collector, the degree of the capacity imbalance determines the high-rate performance.

Figure 15(a) show the results obtained with through-holed/unbalanced LFP cathodes. In contrast with the results with nonholed/unbalanced LFP cathodes, through-holed/unbalanced LFP cathodes exhibited hardly any difference in the high-rate performance compared with the degree of capacity imbalance of LFP cathodes. This was determined from the trend that the data points for the LFP cathodes having different degrees of capacity imbalance almost overlap each other, indicating the cancellation of the negative influence of capacity imbalance on the high-rate performance by through-holing on LFP cathodes [39]. In figure 16, the discharging processes on through-holed, non-through-holed and nonholed and unblanced LFP/LFP cathodes at 0.1 and 10 C are illustrated schematically. The larger discharging capacity retention observed at the through-holed cathodes can be considered to reflect the fact that a facilitated transfer of Li\(^{+}\) ions in the discharging process can occur through both the surface and the sidewalls (produced by forming the through-holes) of the LFP layer (or LFP/current collector layers) [39].
6. Improvement of the high-rate performance of the LFP cathode with a through-holed LFP/AC hybrid electrode structure

As explained above, the holing and through-holing of anodes and cathodes can improve high-rate performance due to the increases in the accessibility of Li$^+$ ions to/from active material layers and material particle surfaces. The decrease in the hole diameter from 20 $\mu$m to several micrometers will lead to a greater improvement in high-rate performance. However, the decrease in the hole diameter has reached a standstill based on a few technicalities of laser through-holing because the decrease in the hole diameter causes an increase in the percentage of loss of active materials on the anodes and cathodes.

The idea of hybrid cathodes of LFP/AC and through-holed cathodes was developed to further improve high-rate performance. The working mechanism of the through-holed LFP/AC hybrid cathodes is shown in figure 17 [40]. After preparing LFP and AC layers on each face of an Al current collector, through-holes with a pore diameter of 22 $\mu$m and an opening rate of 0.5% were formed on the LFP/AC cathodes. A cell was fabricated with a through-holed LFP/AC hybrid cathode and two Li metal anodes. After the cell was fully charged,
Figure 18. Discharge curves of LFP/AC electrodes with 0.5% (a) and 0% (b) of the opening rate of the hole and average hole diameter of 22 µm, and LFP electrode (c) at 20 C, where the discharge of 20 mAh g⁻¹ was repeated seven times and the cells were finally discharged at 0.1 C, with an open circuit time (5 min) inserted between discharge processes. (d) Total discharge capacity observed after 7 discharge/open circuit processes vs the discharge rate. •: LFP/AC electrode with 0.5% opening rate, ▲: LFP/AC electrode with 0% opening rate, ■: LFP electrode. Reproduced with permission from [40].

during the high-rate discharging process of the through-holed LFP/AC cathodes the AC layer was first discharged because of its better high-rate performance than the LFP layer. After the discharging process was performed until the charge corresponding to the capacity that the AC layer had was discharged, the discharging process was stopped, and then the open circuit period was started. During the open circuit period, the energy (electrons) is transferred by the difference in the electrode potential between the AC and LFP layers from the charged LFP layer to the discharged AC layer with the transfer of Li⁺ ions via through-holes from the AC layer to the LFP layer. The AC layer is thus once again charged. The recharged AC layers are discharged again at the high C-rate. A series of these processes of discharge/open circuit (recharging of AC)/discharge/open circuit/… is repeated to discharge the capacity of the LFP/AC hybrid cathode at a high rate of 10–200 C. The through-holes through which Li⁺ ions transfer from the AC layer side to the LFP layer side are essential to recharging the AC layers again. The results of high-rate performance tests with through-holed LFP/AC, nonholed LFP/AC and nonholed LFP cathodes are shown in figure 18

7. Improvement of the energy density of LIBs by prelithiation of graphite anodes using through-holed cathodes and anodes in laminated LIBs

The irreversible capacity, which is observed at the first charge of anodes, is the root cause of the trouble in LIBs because the irreversible capacity decreases the energy density of a LIB cell [41]. To compensate for this irreversible capacity, predoping of Li⁺ ions (prelithiation) into anodes has been proposed using various methods [41] and has been paid increasing attention [42, 43]. High-capacity silicon anodes require prelithiation to improve their low charge/discharge efficiency [44]. The various prelithiation methods proposed have weak points of long treatment time and high cost which should be avoided in the
present mass-production of LIBs. The through-holed structure can also be applied to the prelithiation process and effectively removes the irreversible capacity of all anodes in laminated cells. The process of the prelithiation method using the through-holed structure is described schematically in figure 19 [45]. A laminated cell was constructed with through-holed anodes, cathodes, and separators. A piece of Li metal was arranged near the through-anode, which was located at the end of most of the laminated cells and faced the through-holed anode through the medium of a separator (figure 19(a)). To start the prelithiation process, the Li metal and anodes were electrically contacted until the charge with which prelithiation was applied to all anodes was reached. At the end of the period of the prelithiation process, although the charge that should be reached to intercalate Li$^+$ ions into the layers of anodes was applied to the anodes, the Li$^+$ non-uniformly when compared to the amount of Li$^+$ ions intercalated between anodes because a larger number of Li$^+$ ions were intercalated to the anodes located close to the Li metal and Li$^+$ ions could not reach the anodes that were far from the Li metal (b). The imbalance in the amount of Li$^+$ ions prelithiated among anodes was removed by taking the time to balance the amount of Li$^+$ ions among anodes by electrically contacting all anodes (c). After the balancing period (d), the charging/discharging cycles with the laminated cell were started (e). An examination was made of how much charge and the length of the period for

Figure 19. Schematic of a series of perpendicular predoping, capacity balancing and charging/discharging processes at the laminated cell composed of through-holed anodes and cathodes examined in this study. Reprinted from [45], Copyright (2019), with permission from Elsevier.
the prelithiation and balancing of the intercalated Li$^+$ ions are required to remove the irreversible capacity and to stabilize the charging/discharging capacities during many cycles.

The cyclability of laminated cells in which anodes were prelithiated and balanced versus those that were not prelithiated and balanced was tested with ten charging/discharging cycles. In the case without the prelithiation process, the laminated cells exhibited irreversible capacity at the first charging/discharging cycle. In the case of prelithiation at 6 mAh, the irreversible capacities were much smaller for the laminated cells treated with prelithiation than those without the prelithiation process, and the behavior caused by excessive prelithiation could be observed without regard to the balancing time. Taking into account the excessive prelithiation in figure 20, a charge of 3 mAh was applied to the anodes for prelithiation in the experiments of figure 21. After prelithiation, various balancing times were used. A balancing time of 12 h led to the ideal result of cell lamination; that is, the cell did not exhibit irreversible capacity, excessive prelithiation behavior or deterioration in charging/discharging cycle performance. On the other hand, the balancing time of 6 h was insufficient to stabilize the charging/discharging cycle performance. The charge and balancing time for prelithiation in the laminated cell composed of through-holed anodes and cathodes vary widely in terms of the size of the holes and the hole opening rate. The relationship between the charge and balancing time for the prelithiation and balancing, and the through-hole parameters should be defined to generalize the prelithiation with the through-holed structure.

![Figure 20](image-url)
To evaluate how the prelithiation process was accelerated in the laminated cell composed of through-holed anodes and cathodes, the hole size and opening rate of holes were optimized [46]. In conclusion, the smaller the hole size is at a hole opening rate of 1%, the faster the prelithiation process. In addition, it could be confirmed that an increase in temperature during prelithiation remarkably improves the speed of the prelithiation in the cell designed in this study [34]. As the anodes and cathode for prelithiation in laminated cells, the employment of not only through-holed anodes and cathodes but also anodes and cathodes formed on through-holed current collectors can be considered. Li\(^+\) ions can transfer through anodes and cathodes formed on current collectors because Li\(^+\) ions can move from one side to the other side of anodes and cathodes through dense anode and cathode layers and the holes formed on current collectors. However, the transportation speed of Li\(^+\) on the anodes and cathodes formed on the holed current collector is much lower than that on the anodes and cathodes having through-holes. The speed of prelithiation in the case of a through-holed structure is 3–7 times greater as that in the case of through-holed current collectors [34]. During the prelithiation with the laminated cell composed of through-holed anodes and cathodes, the status of cathodes was checked with the electrode potential and capacity before and after the prelithiation. The fully discharged cathodes inserted between the two anodes during prelithiation, as shown in figure 19, showed a stable potential between 3.3 and 3.4 V (vs Li metal), indicating that charging or processes due to overdischarging do not occur at the cathodes during the prelithiation process in the cell. To confirm again the lack of change in the cathodes in a laminated cell, the cathodes after the prelithiation process were charged at a low C-rate of 0.1 C by pairing with Li metal. The cathodes after the prelithiation process exhibited charging voltage curves and charging capacity similar to those obtained with an as-prepared cathode that was not totally charged. These results indicate that the cathodes inserted between the anodes during prelithiation are not affected by the prelithiation process [47].

8. Conclusion and prospective study

Modification of the structure of anodes and cathodes, which can be applied quickly and effectively to the conventional mass-production process of LIBs, was proposed in this study. The system for making through-holes on anodes and cathodes employs the picosecond pulsed laser, which causes no damage to the anode and cathode layers and forms through-holes by blowing the anode and cathode materials and/or evaporating them, which are then deposited again as solids on the sidewall of the through-holes. The through-holed structure could improve the high-rate performance and energy density of cells and remove performance deterioration caused by the imbalance in the capacity of active material layers formed on both sides of current collectors. The combination of the advantages of LFP cathode materials and AC produced a high-rate performance of the hybrid cathode at a level superior to that of the through-holed cathodes. An original process of prelithiation, in which a laminated cell composed of through-holed anodes and cathodes is improved by removing irreversible capacity, was proposed. Successful results were shown after the optimization of the prelithiated charge applied to anodes and balancing time to equalize the amount of Li\(^+\) ions prelithiated on each anode in the laminated cell. The prelithiation charge, which should be applied to anodes to remove irreversible capacity and to obtain stable charge/discharge capacity, depended on the hole size and hole opening rate formed on the anodes and cathodes, that is, the degree of accessibility of Li\(^+\) ions to/from anode and cathode material surfaces. The factors to accelerate the prelithiation, such as the hole diameter, hole opening rate and temperature, were evaluated by comparing the performance of through-holed anodes and cathodes and anodes and cathodes prepared with a through-holed current collector. Although the parameters such as the hole diameter, hole opening rate and arrangement of holes on anodes and cathodes should be optimized, the improvement of LIB performance, which was introduced in this paper, is worthy of note when compared to that of one of the present LIBs. Therefore,
two directions for work on through-holed structures should be taken for the future. The first direction is the optimization of the parameters in the through-holed structure to increase the improvement in battery performance. As mentioned above, laser technology that can realize a smaller hole diameter should be developed. The formation of smaller holes not having a crater structure on the entrance side of the laser beam will become a key technology. As a second direction, the data to certify the safety of a through-holed structure should be collected carefully. The first bottleneck restraining the practical application of through-holing structures is suspicion from researchers and engineers regarding the safety of cells composed of through-holed anodes and cathodes. For example, it is often pointed out that the adhesion between current collectors and anode and cathode layers is decreased by irradiating the laser beam into the anode and cathode layers. The experiments for evaluating the adhesion property with the peel test were performed with through-holed anodes and cathodes. The adhesion strength of the through-holed LFP cathodes decreased to 95% of that of the nonholed LFP cathodes. The reason for the 5% decrease in adhesive strength after preparing the through-holed structure might be the loss of potential adhesion area caused by the formation of through-holes. Changes in adhesive strength of the through-holed cathodes by several percent are unavoidable in the modification of anodes and cathodes with laser systems. This decrease of several percent should be compensated with the reinforcement of the layer strength of active material layers, for example, by increasing the rate of binder content in active material layers. The second bottleneck is the risk of residual substances might induce ignition and thermal runaway of LIBs. In our system, a dust catcher was added to the system to collect the dust formed during the through-holing. To confirm that all dust was collected with the dust catcher, observation with a stereoscopic microscope and SEM was applied to confirm that all dust could be collected. The confirmation of the absence of dust on the anodes and cathodes treated with the laser system was performed at the laboratory level. In the next step, the confirmation of the safety conferred by dust removal should be validated at the practical level, that is, in the roll-to-roll system with which anodes and cathode are prepared and the through-holing process is applied to anodes and cathodes on the roll-to-roll system. Furthermore, tests of laminated cells constructed with through-holed anodes and cathodes should be conducted with charging/discharging cycles, scratches, impacts, short circuits and high-temperature preservation tests to provide LIBs with a high level of safety.

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