Current Topics in
Electrochemistry
Vol. 21, 2019

Review

Technical review of the method of perpendicular pre-doping of Li$^+$ ions into anodes in lithium ion capacitors and batteries

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ABSTRACT

Recently, the pre-doping of Li$^+$ ions (pre-lithiation) into anodes to compensate for the irreversible capacity loss observed during the first charging cycle has gained much attraction from the viewpoint of improving the energy density of lithium ion batteries (LIBs). Many pre-doping methods such as electrochemical and chemical pre-doping, pre-doping with the help of additives or pre-doping by direct contact with the lithium metal have been proposed. However, the only practical pre-doping method was developed by JM Energy in Japan, which was used to fully pre-dope graphite anodes in lithium ion capacitors (LICs). Although this pre-doping method has high originality and high mass productivity for LICs, it is not well-known to the researchers and engineers in the area of batteries and capacitors. In addition, its information is restrictive because most of the information was written in Japanese. Therefore, in this paper, the details of the practical pre-doping method and its recently-developed related technologies are reviewed. The advantages and disadvantages of the pre-doping method are discussed.

KEYWORDS: lithium ion battery, pre-doping, pre-lithiation, graphite anode, solid electrolyte interphase.

1. Introduction

Lithium ion batteries (LIBs) have recently attracted much attention as a key technology in effective energy utilization for our future mass energy-consuming society [1, 2]. In the charging process of LIBs, Li$^+$ ions are deintercalated from cathode materials and are intercalated into anode materials. In reverse, Li$^+$ ions are deintercalated from anode materials and are intercalated into cathode materials in the discharging process. During the charging/discharging processes, as in the case of playing catch, many Li$^+$ ions are repeatedly exchanged between the anode and cathode. Therefore, LIBs have often been called rocking-chair batteries [3, 4]. If an error occurs in exchanging Li$^+$ ions during the charging/discharging processes (losing the Li$^+$ ions from the system), only the Li$^+$ ions left after loss of the Li$^+$ ions are exchanged between the anode and cathode, that is, the charging/discharging capacity is decreased. The capacity loss cannot be recovered as long as the anode and cathode are paired in the cell. The error usually occurs through a side-reaction during the charging/discharging processes, such as the formation of solid electrolyte interphase (SEI) on the anode surface [5, 6] or decomposition reactions of the anode, cathode, conductive additive, binder, solvent and lithium salt [7-9]. Especially, irreversible capacity loss caused by the formation of SEI during the 1st charging process seriously affects the performance of the cell capacity [10-12]. This loss is becoming increasingly common because the high-capacity anode material silicon requires an improvement of its low charge/discharge efficiency during the first cycle [13, 14]. Pre-doping with Li$^+$ ions (pre-lithiation) to compensate for the Li$^+$ ions moved to the anodes before the capacity loss during the first charging cycle is a

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method to prevent the irreversible capacity loss. Pre-doping methods including electrochemical [15] and chemical [16] pre-doping, pre-doping with the help of additives [17] or pre-doping by direct contact with lithium metal [18] have been proposed in many papers. Placke published an interesting review paper in 2018 on pre-doping methods [19]. In his paper, the pre-doping methods that were proposed in several other papers were classified into the following four categories: electrochemical pre-doping, chemical pre-doping, pre-doping with the help of additives and pre-doping by direct contact with lithium metal. The methods in each category were explained step by step. The particulars of the pre-doping methods are carefully given in his review paper. In this review paper, we would like to discuss practical pre-doping methods that can be applied to the mass production of LIBs and lithium ion capacitors (LICs). As Placke mentioned in his review paper [19], JM Energy (Japan) has developed the first practical pre-doping method for the mass production of LICs [20-23]. Their system was applied to carbon anodes in LICs to lower the anode potential by pre-intercalating Li^+ ions into anode interlayers. Other strategies proposed can be employed to pre-dope Li^+ ions on individual electrodes but are not suitable for the mass production of LICs because they cannot continuously produce pre-doped anodes [19]. In the case of the pre-doping of carbon anodes in the LICs with the perpendicular pre-doping method, un-lithiated anodes, activated carbon cathodes and separators were laminated in a cell, and a lithium (Li) metal foil was set next to the assembly of the anode/separator/cathode/separator/anode…. (Fig. 1) [24]. In order to pre-dope carbon anodes in the LICs where anodes and cathodes are laminated, the Li metal is electrically connected to the anodes with some metal wires or through the medium of the resistor, and then, the pre-doping process was started. The pre-doping process is continued until the anodes are fully pre-doped. All anode and cathode current collectors in the cell have through-holes for the Li^+ ions to pass through and reach all anodes that are located near and far from

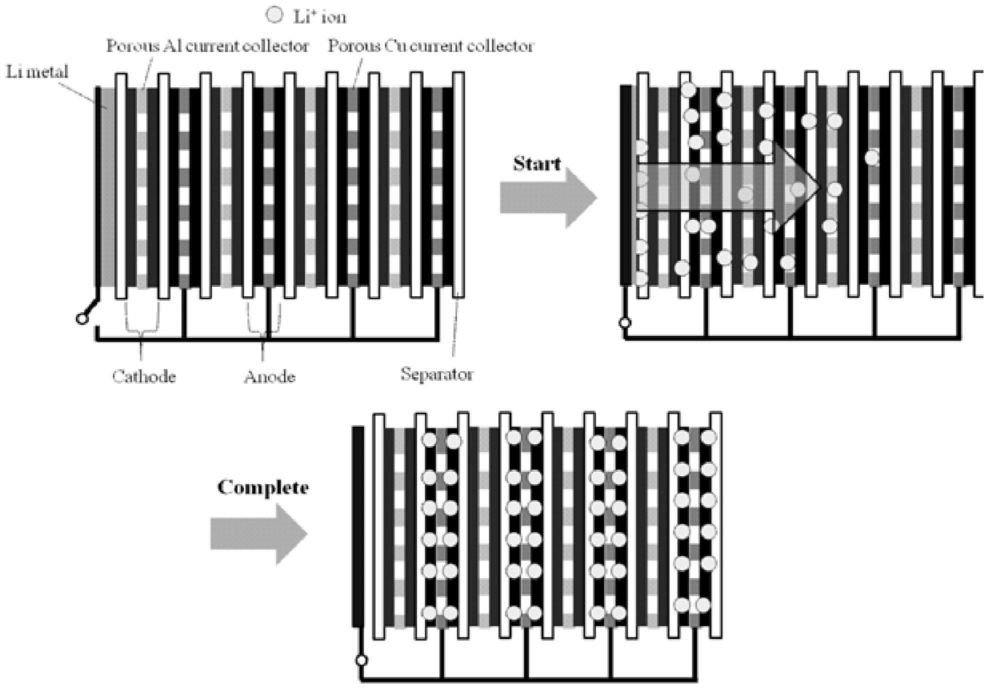

Fig. 1. Schematic description of the perpendicular pre-doping method industrially used in the mass production of LICs, where Li^+ ions are lithiated in laminated carbon anodes during contact of the anodes with a Li metal (Reprinted with permission from Tsuda, T., Ando, N., Haruki, Y., Tanabe, T., Gunji, T., Itagaki, K., Soma, N., Nakamura, S., Hayashi, N. and Matsumoto, F. 2018, ECS Transactions, 85, 1507-1515 (2018). Copyright 2018, The Electrochemical Society.).

the Li metal. Although the Li metal, which has the danger of getting ignited and exploded as a result of its reaction with moisture, is involved in the LIC cells before the pre-doping process, the amount of Li metal placed in the cell is designed to enable the Li metal to be completely dissolved once the pre-doping process is complete. The Li metal set in the cell does not exist in the cell during cell operation. The direction of the transfer of Li^+ ions to intercalate the anodes is perpendicular to the planes of the anodes and cathodes. Therefore, we call the JM Energy's system a perpendicular pre-doping method based on their designation in Japanese. We think that their strategy is the best option for the mass production of LICs and that it is the only pre-doping strategy for the mass production of LIBs, in which irreversible capacity loss can be compensated for in laminated cells. In this paper, the design and performance of the perpendicular pre-doping method will be reviewed. Pertinent factors for the perpendicular pre-doping method to improve the rate of the pre-doping reaction will also be explained from the point of view of its application to mass production. We think that the pre-doping of Li^+ ions into anodes in LIBs with the perpendicular pre-doping method proceeds as shown in Fig. 2. The cell design in LIBs is similar to one in Fig. 1. Li metal foil is set next to the assembly of anode/separator/cathode/separator/anode/…. (1) After the electrolyte solution is injected into the cell, the Li metal is connected to the un-doped anodes, and then, the pre-doping is started. (2) Li^+ ions are formed from the Li metal during the electrochemical oxidation, and the Li^+ ions transfer to the anodes through anodes and cathodes to pre-dope all anodes in the cells. (3) After the charge targeted to pre-dope the anodes flows between the Li metal and anodes, the connection between the Li metal and anodes is cut. (4) The amount of Li^+ ions pre-doped into each anode is different among the anodes in a cell. (5) In order to balance the pre-doped level among the anodes, anodes that have different pre-doped levels are connected to each other to transfer Li^+ ions from the anode that is pre-doped at higher level to one that is pre-doped at a lower level.

2. Perpendicular pre-doping method for fully doping anodes with Li^+ ions in LICs

In the preparation of a LIC cell in which activated carbon cathodes, graphite anodes and separators were laminated, the graphite anodes have to be doped with Li^+ ions into the graphite interlayers to lower the anode potential. Lowering the anode potential induces a large cell voltage, resulting in a higher energy density when compared with electric double layer capacitors. Lithiated anodes are an essential component of LICs. Therefore, how doped anodes are prepared is the most important aspect in the mass production of LICs [23, 25]. As mentioned above, JM Energy has developed the first practical pre-doping method for the mass production

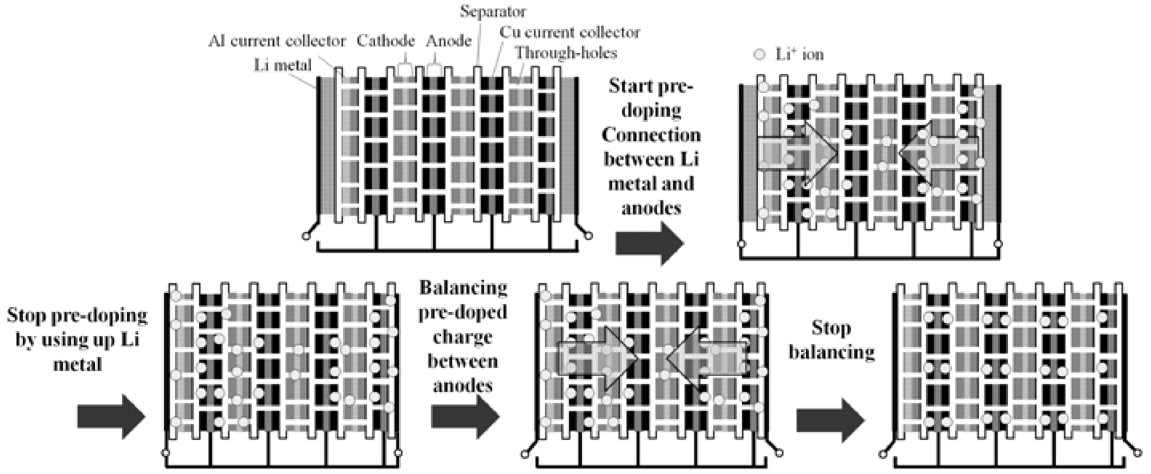

Fig. 2. Schematic description of a series of perpendicular pre-doping and capacity-balancing processes at the laminated cell composed of through-holed anodes and cathodes in LIBs.

of lithium ion capacitors (LICs) [20-23] and actually uses it for the mass production of commercially-available LIC cells. This technology was originally developed by the Subaru Corporation (former name: Fuji Heavy Industry) in Japan. The Subaru Corporation has applied for patents of key technologies in the perpendicular pre-doping method [26-28]. In their patents, in order to shorten the pre-doping period in a laminated cell of LICs, the design of through-holes formed on current collectors for anodes and cathodes was proposed. A protracted pre-doping reaction might lead LICs to critical urgency such as a gas outbreak in a cell and Li dendrite formation as well as lowering of productive efficiency of LICs. Expanded and punched metals were used as the through-holed current collectors. For example, Fig. 3 (A) and (B) show the surface SEM images of punched Cu and Al current collectors produced by the Showa Precision Tools Co. Ltd. in Japan [29]. The Cu and Al foils have an average hole diameters of 330 and 365 μm and hole opening rates of 14 and 17%, respectively. These values of the hole diameter and hole opening rate are the minimum values that can be achieved by punching with a metal mould for mass production. Anode and cathode layers were formed on the punched Cu and Al current collectors. The through-holes were filled with active graphite anode or lithium phosphate oxide (LFP) cathode materials for LIBs (Fig. 3 (C) and (D)). The JM Energy's practical pre-doping method has through-holed current collectors of Cu and Al prepared by punching with metal moulds. The average hole diameter and opening rate are also similar to those of the current collectors shown in Fig. 3 (A) and (B). It was reported that the pre-doping of a laminated cell in which the anodes and cathodes were prepared with the punched current collectors required a pre-doping period of 20-50 hr, and the pre-doping rate exhibited a maximum at a hole diameter of approximately 10 μm [25]. Even after complete pre-doping of all of the laminated anodes, the formation of Li dendrites could not be observed. The reason why the maximum rate of pre-doping could be observed around a hole diameter of 10 μm was attributed to the particle size of the active materials of the anodes and cathodes. The particles of the active materials filled the through-holes, and then, the particles in the through-holes blocked the transfer of Li^+ ions in the cell for pre-doping. In addition, in a patent of the Subaru Corporation, the arrangement of through-holes on current collectors was managed for Li ions to be pre-doped equally on the surface of the anode [26]. For equal pre-doping of an anode surface, the holes on the edge side area of the current collectors were formed with a low opening rate, and alternatively, on the centre area of the current collectors, the opening rate is higher than that on the edge side. When anodes were pre-doped, on the edge side,

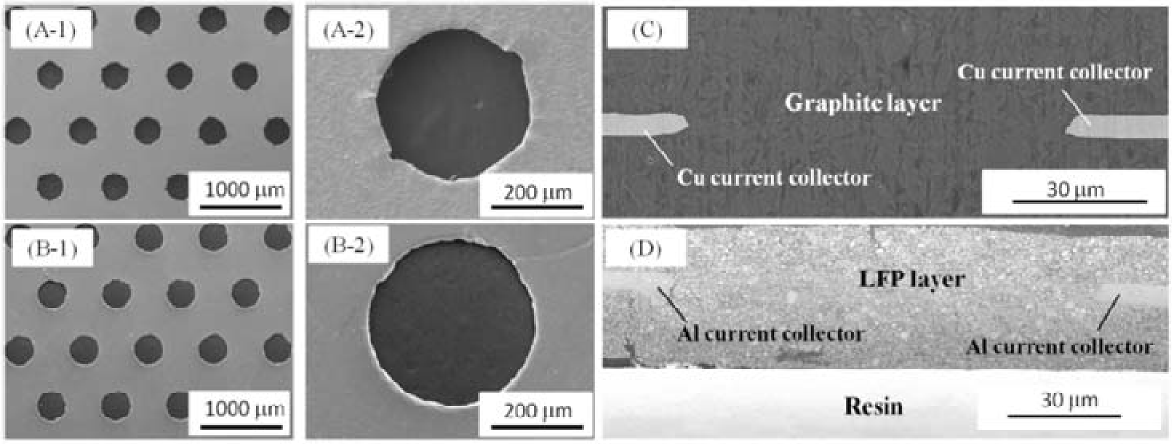

Fig. 3. Surface SEM images of (A) Cu and (B) Al foils punched with a metal and (C, D) cross-sectional SEM images of (C) graphite and (D) LFP layers formed on the punched Cu and Al foils, respectively (Reprinted from Tsuda, T., Ando, N., Matsubara, K., Tanabe, T., Itagaki, K., Soma, N., Nakamura, S., Hayashi, N., Gunji, T., Ohsaka, T. and Matsumoto, F. 2018, Electrochim. Acta, 291, 267-277, Copyright (2018), with permission from Elsevier.).

current concentration usually occurred. The current concentration leads to the formation of Li dendrites. Therefore, in order to not concentrate the current to the edge side of the anodes during the pre-doping process, the opening rate is kept lower at the edge area and higher at the centre area. The transfer of Li^+ ions around the edge area was impeded by decreasing the area for the transfer of Li^+ ions, and then, the current concentration is eased around the edge area of the anodes.

As another method to improve the rate of the pre-doing process, the idea of using the cathodes adjacent to the anodes as a source of Li^+ ions for the pre-doping of anodes was also proposed (Fig. 4) [30-32]. In the first step of this process, the anodes are pre-doped with Li^+ ions intercalated into the cathodes by charging at a constant current with a charging/discharging apparatus. After that, Li^+ ions lost from the cathode materials are compensated for from the Li metal. The rate of transfer of Li^+ ions enhances the large difference in electrode potentials between the Li metal and cathodes.

Recently, Tsuda and co-workers precisely examined the rate of the pre-doping of graphite anodes in the perpendicular pre-doping method [33]. They used a simplified cell composed of through-holed graphite anodes, a separator and Li metal, that is, a cell of Li metal/separator/anode/separator/anode/… (Fig. 5 (A)). Five graphite anodes (ten graphite layers because the graphite layers were coated on both sides of the current collector) were laminated in the cell. The through-holed copper foils prepared with a pico-second pulsed laser were used as current collectors for preparing the anodes (Fig. 5 (B)). The through-holed current collectors were prepared with a pico-second pulsed laser system developed by the Wired Co. Ltd. in Japan. They have already developed a laser system that can produce holes on Al and Cu foils at 300,000 holes sec^{-1} [34]. The average hole diameter and opening rate that they can produce are 3-5 μm and 1% at a minimum, respectively. The graphite anodes were prepared with graphite (SMG-N-HE2-20, Hitachi Chemical Company, Ltd., Japan), vaper grown carbon fibber (VGCF, VGCF®-H, Showa Denko K.K., Japan), carboxymethyl cellulose (CMC, Polyscience Inc., cat.# 6139) and styrene-butadiene rubber (SBR, S2910(J)-1, JSR Corporation, Japan) with a ratio of the weight % of graphite:VGCF:CMC:SBR = 91:5:2:2. The graphite layers were coated on the through-holed current collectors. The thickness of a graphite layer on the current collector was 77 μm. The density of a graphite layer was 0.50–0.52 g cm^{-3}. The sizes of the graphite anodes and Li metal were 34 mm x 20 mm. A separator sheet (HiporeTM, Asahi Kasei Co., Japan, thickness: 25 μm; size: 37 mm x 23 mm) was inserted between the electrodes. An electrolyte solution was

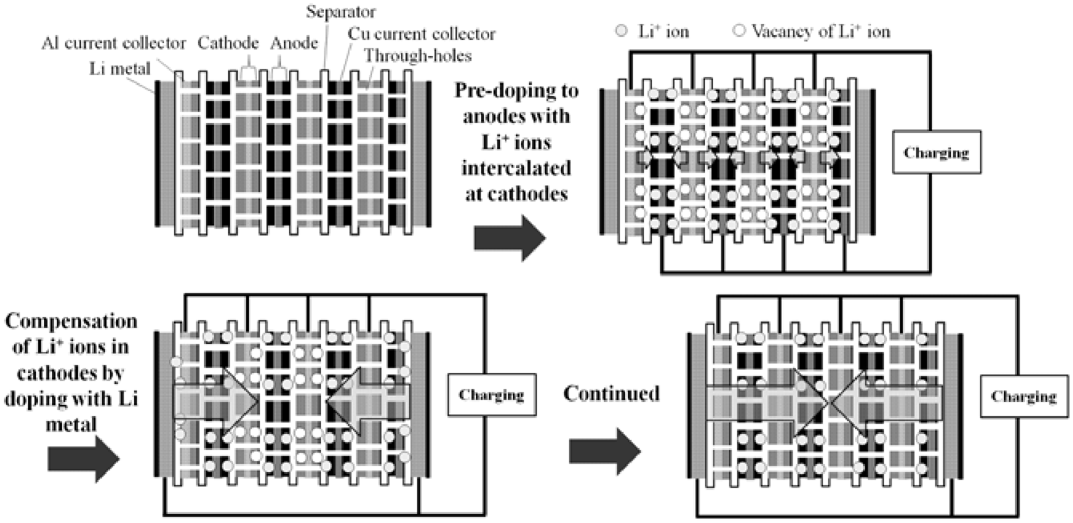

Fig. 4. Schematic description of a series of perpendicular pre-doping methods with cathodes to improve the rate of pre-doping.

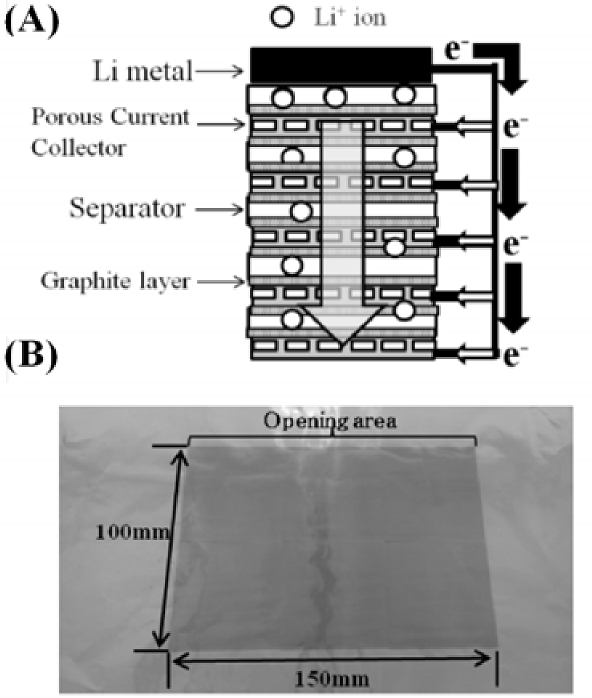

Fig. 5. (A) Schematic description of a cell for the pre-doping reaction with the graphite layer/through-holed current collector anodes and Li metal and (B) micrograph of a prepared through-holed copper current collector (Reproduced from Tsuda, T., Inami, Y., Nakamura, R., Ando, F., Mochizuki, Y., Gunji, T., Tanabe, T., Kaneko, S., Itagaki, K., Soma, N. and Matsumoto, F. 2017, Electrochemistry, 85, 186-194 with permission from ECSJ.).

utilized, consisting of 1 M $LiPF_6$ in ethylene carbonate:dimethyl carbonate = 1:1 (v/v) + vinylene carbonate (2.7 wt%) mixture (Ube Chemicals, Japan). The pre-doped charge of each graphite anode in a cell was evaluated by discharging the anode in a half cell of the pre-doped anode with Li metal as a counter electrode. The rate of pre-doping in the cell was evaluated based on the number of fully pre-doped anodes in the cell after the pre-doping periods of 20, 40 and 60 hr (Fig. 6). From the data in Fig. 6, it can be seen that full pre-doping of five anodes in the cell required a pre-doping period of 60 hr with a through-hole diameter of 5 μm at 25 °C. The through-hole diameter of 5 μm is the optimal value to shorten the pre-doping period of anodes. A decrease in the through-hole diameter to less than 5 μm might cause a slowdown of the pre-doping process due to the reasons mentioned above [25]. The rate of the pre-doping process was improved by adjusting the reaction temperature for the pre-doping. It was confirmed that the reaction temperature could be increased to 65 °C to improve the rate of the pre-doping process in the perpendicular pre-doping method [25].

As another electrochemical pre-doping method, which is opposite to the perpendicular pre-doping method, a vertical pre-doping method, in which the plane of the Li metal is placed in parallel with the planes of the paired anode and cathode, has also been proposed and examined for the pre-doping of Li^+ ions in a cell [35]. Mitsuda examined the vertical pre-doping method with an eight-reference electrode system developed originally by them. As shown in Fig. 7, the anode and cathode were overlapped in the centre of the test cell system. A Li metal was set in the neighbourhood of the carbonaceous anode. The anodes and Li metal were short-circuited, and the current flowing between the anode and Li metal was measured. The potentials of the anode were measured during the pre-doping process with the eight-electrode reference system, whose eight reference electrodes were arranged around the anode. The potential of the anode decreased gradually from near the Li metal to the end of the anode. In addition, the potentials in the horizontal plane of the anode did not become uniform even after 60 hr. A slight current between the anode and Li metal could be observed even after 60 hr. These results indicate that the vertical pre-doping method requires a larger pre-doping period than perpendicular pre-doping method. Complete pre-doping of an anode in an anode and cathode pair composed of through-holed current collectors with Li metal, which is located at the same distance from the anode as for the vertical pre-doping method, requires less than 10 hr (the period in the perpendicular pre-doping method was measured by the author’s experiment).

As far as other attempts to pre-dope anodes with the perpendicular pre-doping method, there are several examples reported in papers. For instance, Sivakkumar examined the pre-doping of Li^+ ions into graphite anodes with a Li/graphite/AC three-electrode cell, in which the graphite anode was prepared with copper mesh [36]. In the results of pre-doping upon short circuiting between the Li metal and graphite anode, the time taken for the Li/graphite potential to reach 0.05 V indicating

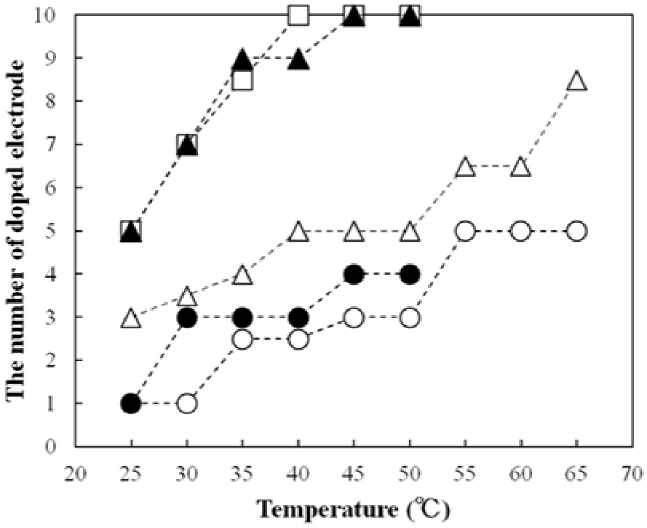

Fig. 6. Dependence of the number of doped graphite layers in the graphite/through-holed Cu current collector anodes, which were laminated, after the pre-doping reaction for 20 (○,●), 40 (Δ,▲) and 60 (□) h on the reaction temperature. The opening rates of pore on the Cu current collectors are 1(○,Δ, □) and 4(●,▲)% (Reproduced from Tsuda, T., Inami, Y., Nakamura, R., Ando, F., Mochizuki, Y., Gunji, T., Tanabe, T., Kaneko, S., Itagaki, K., Soma, N. and Matsumoto, F. 2017, Electrochemistry, 85, 186-194 with permission from ECSJ.).

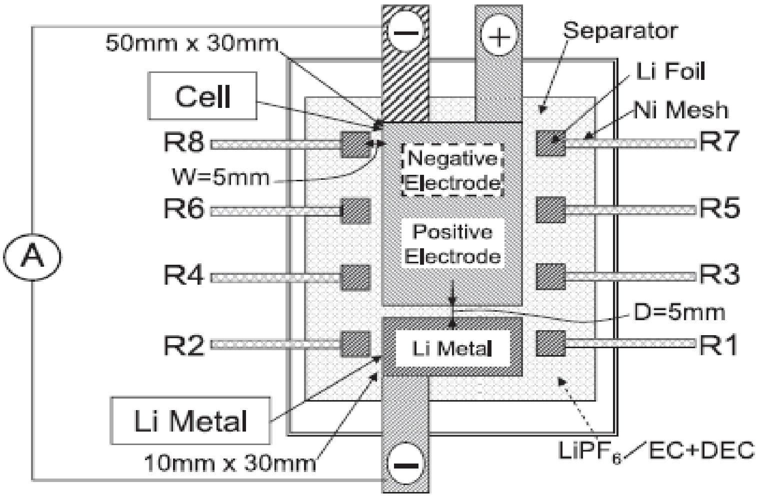

Fig. 7. Plane view of a LIC (LIB) cell with a lithium metal electrode and eight-reference electrodes (Reproduced from Mistuda, K. and Takemura, D. 2010, Electrochemistry, 78, 606-610 with permission from ECSJ.).

the end of the complete doping process was observed to be ~10 h irrespective of the amount of graphite. The amount of Li$^+$ ions doped into the graphite anode after 30 h was estimated to be equivalent to 81% of the theoretical capacity of graphite (theoretical capacity of graphite: 372 mAh g^{-1} (100%)). The amount of Li$^+$ ions doped was evaluated by discharging the anode with Li metal as the counter electrode after the pre-doping. Full pre-doping could not be completed with the pre-doping method.

Gourdin compared the following three pre-doping methods (Fig. 8) [37]: the first one mimics the direct contact between a Li metal and carbon anode, the second one is electrochemical pre-doping with

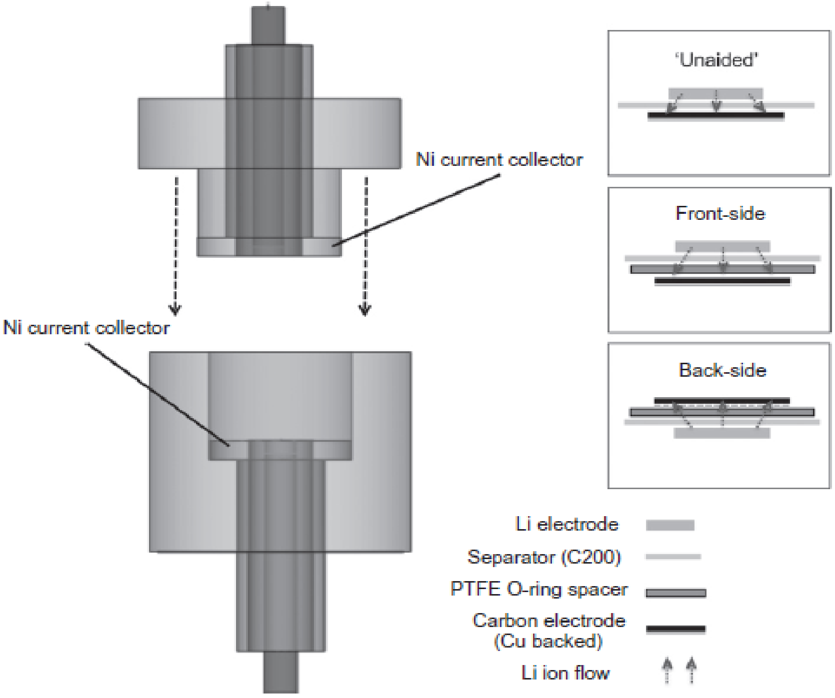

Fig. 8. Schematic illustration of the evaluation cell (Reprinted from Gourdin, G., Smith, P. H., Jiang, T., Tran, T. N. and Qu, D. 2013, J. Electroanal. Chem., 688, 103-112, Copyright (2013), with permission from Elsevier.).

the front-side configuration of the arrangement of Li metal and the carbon anode; and the last one is electrochemical pre-doping with the back-side configuration. The Li metal and carbon anode were arranged such that the Li metal electrode faced the Cu mesh or "back" side of the carbon anode. From the results obtained from the comparison of the three configurations, the difference in the SEI layer and charge-transfer resistances of the carbon anode could not be observed between the front- and back-side configurations after pre-doping. An advantage of performing the doping in the electrochemical front- and back-side configuration is that the method apparently produces a thinner or less dense SEI layer, which would minimize the impact on the migration of Li^+ ions through the layer to and from the carbon anode surface during the cycling of the cell. The electrochemically-driven doping of the front- and back-side insertion method can significantly shorten the time to form the doped anode, as compared to mimics of the direct contact of Li metal with the anode. There was no drawback with the use of the back-side configuration when compared with the front-side configuration. The back-side configuration could significantly decrease the electrode preparation time because the back-side configuration can remove the need to disassemble the cell to rearrange its internal configuration before it can be operated in its normal mode, which would have great benefits for the development of these devices. It was also reported that direct contact between graphite and Li metal for pre-doping led to the formation of a thick SEI that weakens the adhesion of active materials and the current collector and produced electrical resistance as well as electrical contact loss between the active materials and current collector [38]. Electrochemical pre-doping played an important role in the enhancement of the electrochemical performance of a SiO_x electrode. The electrochemical pre-doping was effective for the formation of SEI layers not only on the surface of the electrode but also in the electrode without vacancies and boundaries [39]. Kumagai examined the optimal electrochemical pre-doping level of a graphite anode in a LIC. The high specific capacitance and the best cycle performance were accomplished at a pre-lithiation level of 71.1% based on the theoretical Li intercalation capacity of graphite. Although higher pre-lithiation levels of 89.0% contributed to the high specific capacitance in early cycling, they allowed a considerable decrease in the specific capacitance at higher numbers of cycles [40].

3. Acceleration of the pre-doping reaction in the perpendicular pre-doping method

As mentioned above, in order to accelerate the pre-doping reaction in a laminated cell in LIBs and LICs, the design of the holes formed on the current collectors, anodes and cathodes should be examined more thoroughly. Tsuda and co-workers developed the technology for through-holing of current collectors [41], anodes and cathodes [29] with a pico-second pulsed laser to accelerate the transfer of Li^+ ions into the cells of LIBs and LICs during the pre-doping of Li^+ ions into graphite anodes. With the laser system as shown in Fig. 9 [29], the through-holes having a hole diameter of 20 μm and an opening rate of 0.5-1.0 % could be formed on anodes and cathodes. The holes were arranged in a grid pattern on the graphite anodes and $LiFePO_4$ cathodes. The surface scanning electron microscopy (SEM) images in Fig. 10 show grid patterns on anodes and cathodes [41]. The opening rate (R_{opening}) of holes formed on anodes and cathodes is defined as the percentage of the holed area calculated by eq. (1).

$$R_{\text{opening}}\ (\%) = (A_{\text{hole}}) / (A_{\text{unit part}}) \times 100 \qquad (1)$$

where A_{hole} and $A_{\text{unit part}}$ are the areas of a hole and a unit part of a grid patterned on the anode and cathode. From the cross-sectional SEM images of the through-holed anode and cathode, it can be observed that the holes formed have tapered shapes because the active materials on the anode and cathode were blown off from the surface of the anode and cathode by the impact of the strong incidence of a laser. On the side where the laser hits, a large hole diameter and high degree of tapering could be observed at both the anode and cathode (Fig. 11) [41]. It was also confirmed that the graphite layer was not decomposed by the incidence

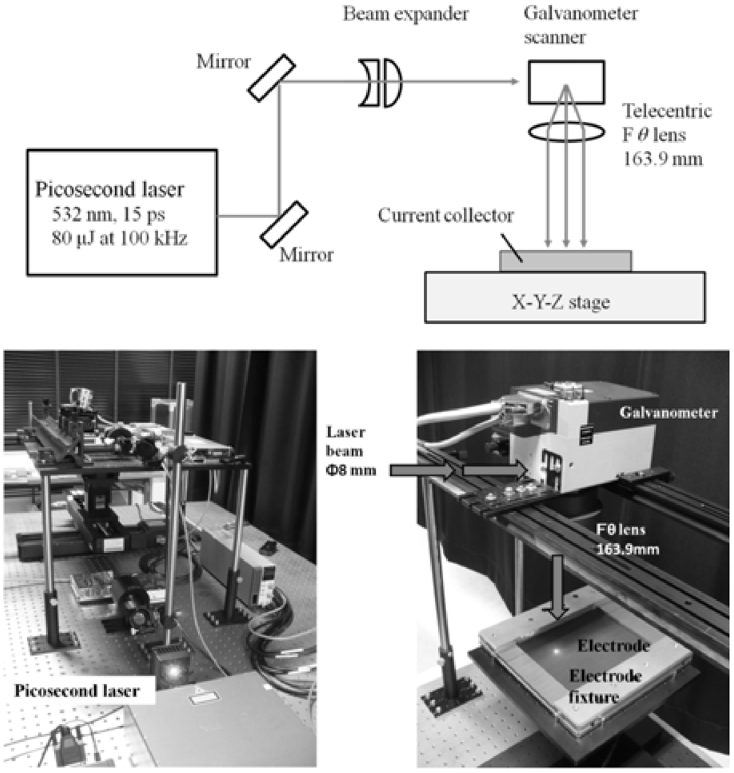

Fig. 9. A schematic description of the preparation system of through-holed anodes and cathodes with a pico-second pulsed laser and a galvanometer scanner system (Reprinted from Tsuda, T., Ando, N., Matsubara, K., Tanabe, T., Itagaki, K., Soma, N., Nakamura, S., Hayashi, N., Gunji, T., Ohsaka, T. and Matsumoto, F. 2018, Electrochim. Acta, 291, 267-277, Copyright (2018), with permission from Elsevier.).

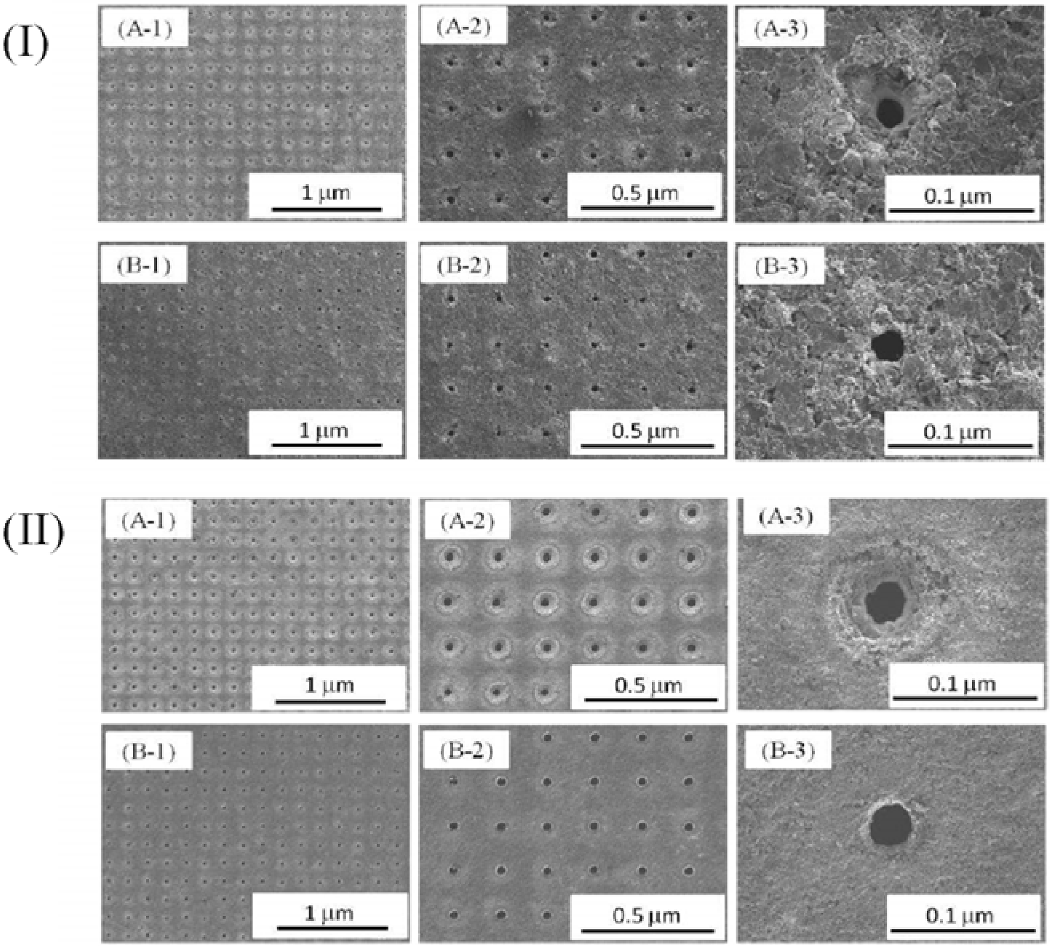

Fig. 10. SEM images of through-holed (I) graphite anodes and (II) $LiFePO_4$ cathodes. (A) The view from the incident laser plane and (B) the view from the laser emission plane. The opening rate was 1 %. The average hole diameter was 20 μm (Reprinted with permission from Tsuda, T., Ando, N., Mitsuhashi, N., Tanabe, T., Itagaki, K., Soma, N., Nakamura, S., Hayashi, N. and Matsumoto, F. 2017, ECS Transactions, 80, 1391-1397 (2017). Copyright 2017, The Electrochemical Society.).

of the laser on the graphite layer with Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) (Fig. 12). The G/D peak ratio observed from graphite layers with Raman spectroscopy (I) did not change before and after incidence of the laser on the graphite surface to prepare the through-holes. In addition, the peak area ratio for C-C and C=O bonds in the XPS spectra (II) observed with the graphite layers also did not change before and after the incidence of the laser. The incidence of the laser did not cause damage to the graphite materials [42]. Additionally, in the through-holed anodes and cathodes, the rate of the pre-doping reaction was examined with the laminated cell of through-holed anodes and Li metal as shown in Fig. 5. Fig. 13 shows the dependence of the number of doped through-holed graphite in the laminated cell for a certain pre-doping period on the hole diameter. From the comparison of the results obtained with through-holed graphite and un-through-holed graphite anodes prepared with a through-holed current collector, it can be seen that the through-holing of the anodes could remarkably shorten the pre-doping period. When a hole diameter of 5 μm was formed on the anode surfaces, under 25 °C, full pre-doping of ten graphite layers could be finished in 20 h, while only four graphite layers could be pre-doped in 20 h without through-holes. Through-holing to speed up the pre-doping reaction was very effective. The

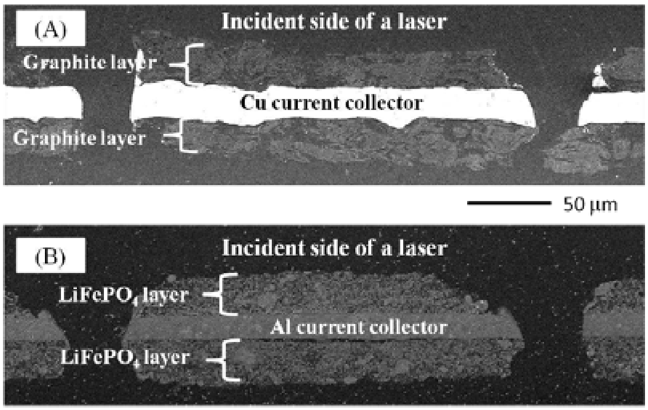

Fig. 11. Cross-sectional SEM images of the through-holed (A) graphite anode and (B) LiFePO$_4$ cathode. The opening rate was 1%. The average hole diameter was 20 μm (Reprinted with permission from Tsuda, T., Ando, N., Mitsuhashi, N., Tanabe, T., Itagaki, K., Soma, N., Nakamura, S., Hayashi, N. and Matsumoto, F. 2017, ECS Transactions, 80, 1391-1397 (2017). Copyright 2017, The Electrochemical Society.).

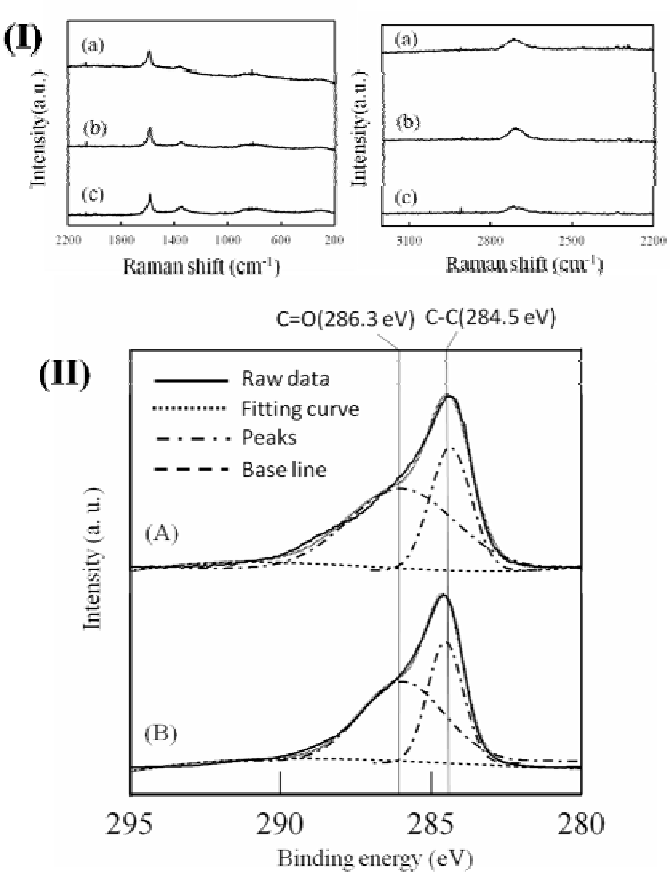

Fig. 12. (I) Raman spectra of (a) graphite near the hole on the graphite electrode (opening rate of holes on the electrode: 1%; hole size: 50 μm), (b) graphite deposited on the Cu current collector and (c) graphite powder. (II) XPS spectra of a (A) through-holed graphite layer and (B) non-through-holed graphite layer on anodes (Reprinted from Tsuda, T., Ando, N., Mitsuhashi, N., Tanabe, T., Itagaki, K., Soma, N., Nakamura, S., Hayashi, N. and Matsumoto, F. 2018, Electrochemistry, 86, 10-18 (2018) with permission from ECSJ.).

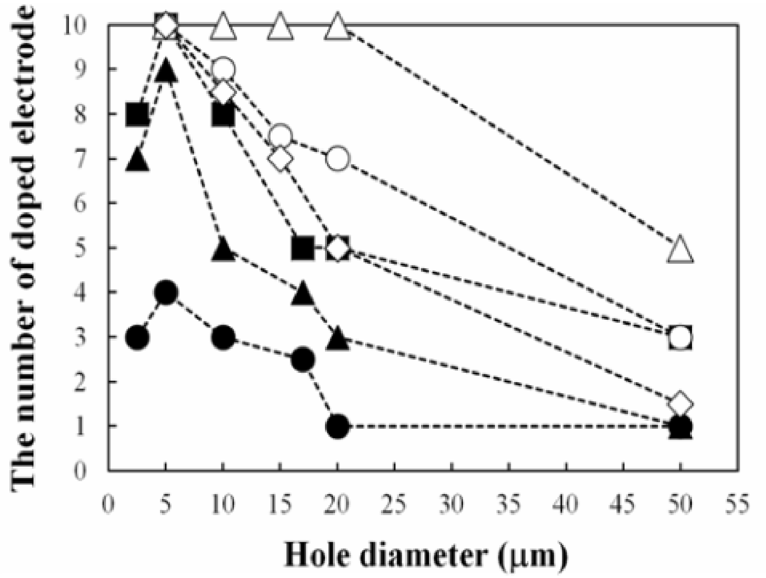

Fig. 13. Dependence of the number of doped through-holed graphite (◊, ○, Δ) and graphite/through-holed Cu current collector (●, ▲, ■) anodes, which were laminated, after the pre-doping reaction for 15 (◊), 20 (○, ●), 40 (Δ, ▲) and 60 (■) h on the average hole diameter on the graphite layer and current collector at 25 °C. The opening rates of holes on the graphite and Cu current collectors are 1% (Reprinted from Tsuda, T., Ando, N., Mitsuhashi, N., Tanabe, T., Itagaki, K., Soma, N., Nakamura, S., Hayashi, N. and Matsumoto, F. 2018, Electrochemistry, 86, 10-18 (2018) with permission from ECSJ.).

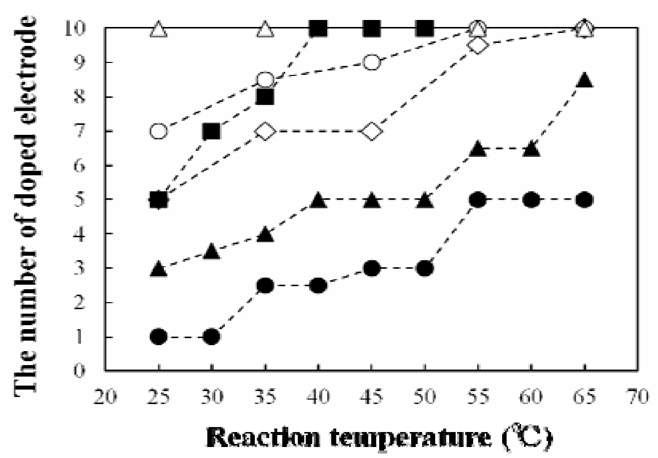

Fig. 14. Dependence of the number of doped electrodes in the porous graphite (◊, ○, Δ) and graphite/porous Cu current collector (●, ▲, ■) anodes (average hole diameter on the graphite layer and current collector: 20 μm), which were laminated, after the pre-doping reaction for 15 (◊), 20 (○, ●), 40 (Δ, ▲) and 60 (■) h on the reaction temperature. The opening rates of holes on the graphite and Cu current collectors are 1% (Reprinted from Tsuda, T., Ando, N., Mitsuhashi, N., Tanabe, T., Itagaki, K., Soma, N., Nakamura, S., Hayashi, N. and Matsumoto, F. 2018, Electrochemistry, 86, 10-18 (2018) with permission from ECSJ.).

temperature dependence of the pre-doping reaction was also examined with the same cell design [42]. With a hole diameter of 20 μm and hole opening rate of 1%, an increase in the reaction temperature accelerated the reaction rate. The reaction rate at 65 °C was 2 to 3 times the rate at 25 °C (Fig. 14). The pre-doping period of 20 h is equal to the one observed with the laminated cell of graphite/through-

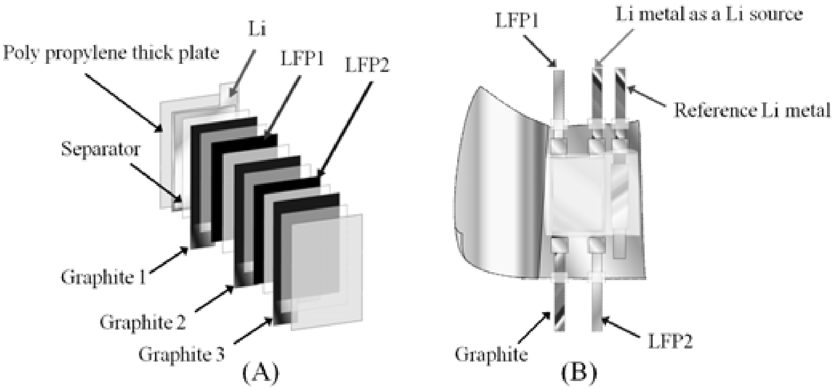

Fig. 15. Schematic of a cell in the pre-lithiation reaction with porous graphite, LFP electrodes and Li metal: (A) electrode assembly and (B) laminated packaging design. The connectors of three graphite electrodes (Graphite 1-3) are shown to be assembled in (B) (Reprinted with permission from Tsuda, T., Ando, N., Haruki, Y., Tanabe, T., Gunji, T., Itagaki, K., Soma, N., Nakamura, S., Hayashi, N. and Matsumoto, F. 2018, ECS Transactions, 85, 1507-1515 (2018). Copyright 2018, The Electrochemical Society.).

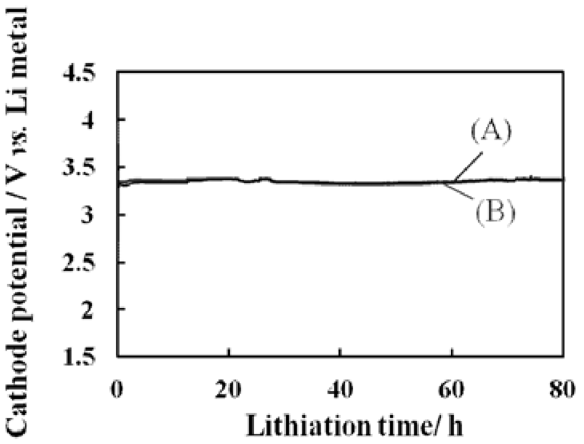

Fig. 16. Time course of the electrode potentials of the cathodes inserted between anodes during lithiation. (A) LFP1 and (B) LFP2 electrodes are shown in Fig. 14 (Reprinted with permission from Tsuda, T., Ando, N., Haruki, Y., Tanabe, T., Gunji, T., Itagaki, K., Soma, N., Nakamura, S., Hayashi, N. and Matsumoto, F. 2018, ECS Transactions, 85, 1507-1515 (2018). Copyright 2018, The Electrochemical Society.).

holed current collector anodes and Li metal, as shown in Fig. 5. Additionally, from these results, the effect of through-holing the anodes on the reaction rate can be understood numerically.

The perpendicular pre-doping with a laminated full cell of through-holed anodes and cathodes was also examined by Tsuda and co-workers [24]. They evaluated the status of cathodes inserted between pre-lithiated anodes during the pre-doping. The change in the electrode potential of the cathodes was monitored with the cell shown in Fig. 15. When the pre-doping process was started, the Li metal as a Li source was connected to the anodes in the assembly of the anodes and cathodes, with the connectors tied up in the pack. Each connector for two LFP cathodes (LFP1 and LFP2) was connected to a voltage meter, and the cathode potentials of LFP1 and LFP2 were measured against a reference Li metal electrode, which was located next to the assembly of anodes, cathodes, Li metal and separators. Fig. 16 shows the change in the electrode potential for the cathodes LFP1 and LFP2 during the pre-doping process. For a pre-doping period of 80 h, the LFP1 and LFP2 electrodes showed a stable potential between 3.3 and 3.4 V (*vs.* Li metal). In order to confirm the status of the cathodes more thoroughly, after the pre-doping process for 80 h, two cathodes were charged independently at a constant current after pairing each LFP cathode with Li metal as a half-cell after the pre-lithiation. The cathodes of LFP1 and LFP2 exhibited a charging capacity of 150 mAhg^{-1}, which was equal to the theoretical capacity of the LFP. These results also indicate that charging or over-discharging processes did not occur at the cathodes during the pre-doping process in the laminated cell and that the cathodes inserted between the anodes during pre-lithiation are not affected by the pre-lithiation process [24].

4. Conclusions and perspective

In this review paper, the perpendicular pre-doping method for anodes in LIBs and LICs was reviewed. This method was developed and used by JM Energy to produce commercially available LICs. Although many pre-doping methods have been proposed in several papers until now, those methods have some problems regarding their application in mass production. The perpendicular pre-doping method also has some problems in that the current collectors for Li metal and separator sheets, which are used to separate the Li metal and an anode (or cathode), are left in the cell after the pre-doping process and the space left for the current collectors and separators decreases the volumetric energy density of the cell. Additionally, through-hole current collectors are expensive, and through-holed current collectors, anodes and cathodes are mechanically weak. The volumetric energy density loss due to the space left by the current collector and separator is unavoidable. However, the space that causes the capacity loss can be minimized by decreasing the thickness of the current collector and separator. The price of through-holed current collectors, anodes and cathodes will become lower once they are introduced into mass production. The laser technology developed recently and mentioned in this paper will reach a level that is applicable to mass production, that is, it can be applied to the roll-to-roll process in the production of anodes and cathodes for LIBs and LICs. The mechanical strength of current collectors, anodes and cathodes are not decreased by through-holing to anodes and cathodes because the arrangement and hole size are devised to not decrease their strength.

As mentioned above, the most important point for the perpendicular pre-doping method to be accepted by the LIB and LIC industries is speeding up of the process of through-holing in current collectors, anodes and cathodes. In addition, the pre-doping should occur with equal doping levels on the anode and cathode surfaces. High speed technology for the formation of through-holes will be achieved by refining the conventional technology and the development of new technology. Additionally, the optimization of the hole size, opening rate and arrangement for the shortest pre-doping period should be determined. These points have not been satisfactorily examined yet. As a last important point of the preparation of through-holes, the dusts of current collector and active materials, which were produced during the through-holing process, should be completely removed from the anode and cathode surfaces. The dusts left on the anode and cathode surfaces might become the cause of ignition of the LIB and LIC. A dust monitoring and removal system should be developed with the development of through-holing technology. The optimization of these apparatus will disseminate the perpendicular pre-doping method for its employment in the mass production of LIBs and LICs by many manufacturers. Although there are many results obtainable for the perpendicular pre-doping method, in which the three electrodes including an anode, cathode and Li metal were assembled and the anode was pre-doped with the Li metal, there are only a few results available for the laminated assembly of through-holed anodes and cathodes along with Li metal. In order to make a decision whether the perpendicular pre-doping can be actually applied in mass production, the details of the pre-doping reaction with the through-holed electrode assembly on a practical level should be analysed, and the performance should be compared with those of other pre-doping methods.

ACKNOWLEDGEMENTS

This work was financially supported by the Light Metal Educational Foundation, Inc. in Japan.

CONFLICT OF INTEREST STATEMENT

There are no conflicts of interest.

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