

The Current Situation and Problems of Rechargeable Lithium Ion Batteries

Masashi Kotobuki

Department of material and environmental engineering, Hakodate National College of Technology Tokura 14-1, Hakodate, 042-8501, Hokkaido, Japan

Abstract: Lithium batteries have been widely used as a power source for numerous small devices such as mobile phones and laptop computers. Recently, the lithium battery is expected to be used as a power source for electric vehicles. For the electric vehicles application, an improvement of energy and power densities and safety is required. In this review, a brief explanation of structure and mechanism of the lithium batteries are given at first. Then, recent researches on cathode and anode materials to improve the energy and power densities are described. Some studies on solid electrolyte and all-solid-state battery are also introduced.

Keywords: Li battery, Solid electrolyte, All-solid-state battery, Ceramics materials.

1. INTRODUCTION

Since the lithium ion battery first appeared in 1991, it has been widely used as a power source, especially in mobile electronic devices [1]. It is expected that the lithium ion battery will be used as a power source for electric vehicles, electric motor cycles, and the smart grid system. Production of these lithium ion batteries has increased year after year, as shown in Fig. (1) [2]. The lithium ion battery occupies a vital portion of the greater battery industry.

Before the advent of the rechargeable lithium ion battery, the lithium primary battery, with lithium metal anode, was available on the market. Many researchers have challenged the development of the rechargeable lithium battery by further development of the lithium metal anode of the lithium primary battery; however, they have not been able to overcome the safety problems, mainly due to the dendritic deposition of Li metal during the charging process [3]. The rechargeable lithium ion battery was developed using carbonaceous compounds instead of lithium metal as the anode. At the anode, lithium exists in its ionic state, and consequently, the rechargeable lithium battery is called a "lithium ion battery". Currently, there is much ongoing research to improve its performance and safety. Herein, recent researches on anode, cathode, and electrolyte materials are described.

2. ELECTRODE REACTIONS OF THE LITHIUM ION BATTERY

Fig. (2) depicts the reactions at the electrodes of lithium ion batteries [4], where LiCoO_2 and graphite are used as

materials for the cathode and anode, respectively. An electrolyte and separator must be placed between the anode and cathode, although they have been omitted in the figure for clarity. The electrodes are generally made of three components: an active material, an electronic conducting material, and a binder. These three components are mixed with a solvent to prepare a slurry, which is then painted onto a current collector. Al and Cu foils are typically used as current collectors for the cathode and anode, respectively. In general, the thickness of the electrode is approximately below 100 μm .

In the case of lithium ion battery consisting of LiCoO_2 cathode and graphite anode, the battery is constructed in a discharged state; all of the lithium ions are contained at the cathode, whereas the graphite anode does not contain any lithium ions. Thus, a charging process is required before use.

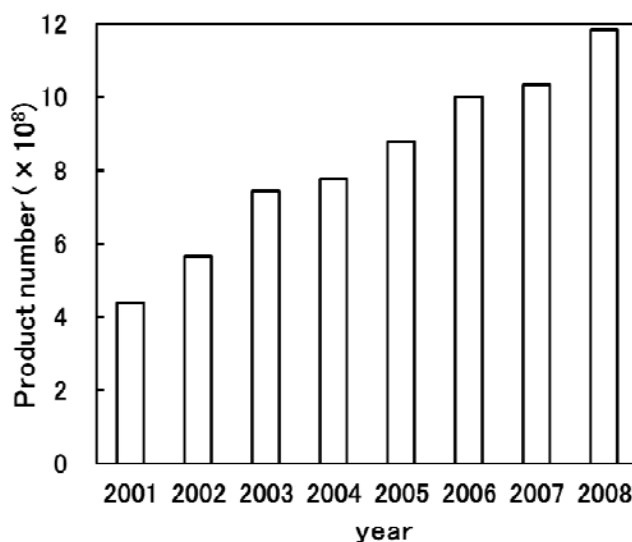


Fig. (1). Production of lithium ion batteries.

*Address correspondence to this author at the Department of material and environmental engineering, Hakodate National College of Technology, Tokura 14-1, Hakodate, 042-8501, Hokkaido, Japan; Tel: +81-138-59-6466; Fax: +81-138-59-6466; E-mail: kotobuki@hakodate-ct.ac.jp

During the charging process, the oxidation and reduction reactions proceed at the cathode and anode, respectively. The Co^{3+} in the LiCoO_2 cathode is oxidized to Co^{4+} , and an electron goes to the anode through a current collector and then through an external circuit. During this process, lithium ion (Li^+) is released into the electrolyte. At the other electrode, Li^+ ion from the electrolyte and electron from the external circuit, get transferred to the graphite anode. During the discharge process, these reactions are reversed. Consequently, lithium ion battery reactions proceed by moving only Li ion and electron. These battery reactions are very simple when compared to other batteries, where they usually include a reaction of the electrode with the electrolyte. This simple reaction implies that all materials that can release and insert lithium ions reversibly have the potential to become candidates for lithium ion battery electrode materials and that the development of these materials would allow to construct lithium ion batteries with better performance.

3. DEVELOPMENT OF ELECTRODE ACTIVE MATERIALS

The most important aspect for the development of high performance lithium ion batteries is research and development regarding the materials that comprise the battery. Many researchers have previously reported on the use of metal, ceramic, polymer, liquid, and gel materials for electrodes, electrolytes, separators, etc. Herein, the use of ceramics materials for lithium ion batteries is described.

3.1. Cathode materials

LiCoO_2 has been used as a cathode material for a long time, and many researchers have focused on the development of new cathode materials to improve the energy density and safety of lithium ion batteries [5].

Some researchers have addressed the energy capacity of the cathode and have tried to improve it using LiNiO_2 [6], $\text{LiNi}_{0.8}\text{Co}_{0.2}\text{O}_2$ [7], $\text{LiNi}_{1/3}\text{Mn}_{1/3}\text{Co}_{1/3}\text{O}_2$ [8, 9], or $\text{LiNi}_{0.5}\text{Mn}_{0.5}\text{O}_2$ [10]. These materials consist of a layered structure, similar to the original LiCoO_2 . As shown in Fig. (3), the voltage at the Li^+ intercalation/deintercalation is changed by substitution of other transition metals for Co[11]. When the charge voltage is high, oxidation of the electrolyte occurs at the cathode, causing gas generation and swelling of the battery [12]. In such a state, the battery becomes unsafe and the performance is completely different from its original state. For this reason, present commercial lithium ion batteries are restricted to a charging voltage of 4.2 V. In the case of the LiCoO_2 cathode, the formation of $\text{Li}_{0.5}\text{CoO}_2$ is responsible for this 4.2 V charging limit. Thus, the capacity of the cathode is limited to 120 ~ 140 mAh g^{-1} . The active materials mentioned above have been developed in an attempt to overcome this issue.

LiNiO_2 is an ideal material because of the low cost of Ni and its high theoretical capacity; however, poor reversibility against Li^+ intercalation/deintercalation still remains a problem [13]. Other materials have been reported with relatively stable reversibility and a capacity of 170 ~ 200 mAh g^{-1} . Unfortunately, this capacity is not high enough for the next generation batteries, such as those used in electric vehicle applications, which require a capacity of 250 ~ 300 mAh g^{-1} .

Li-containing transition metal oxides, with a composition of Li_2MO_3 , have been anticipated as a high-capacity cathode material [14,15]. These materials contain two Li^+ atoms in its crystal, implying that it should possess high capacity. Charge and discharge curves of $\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_3$ are depicted in Fig. (4) [16]. The reported discharge capacity was near 300 mAh g^{-1} , which almost achieves the desired value.

Another strategy for improving the energy density of the cathode is the use of higher charge and discharge voltages.

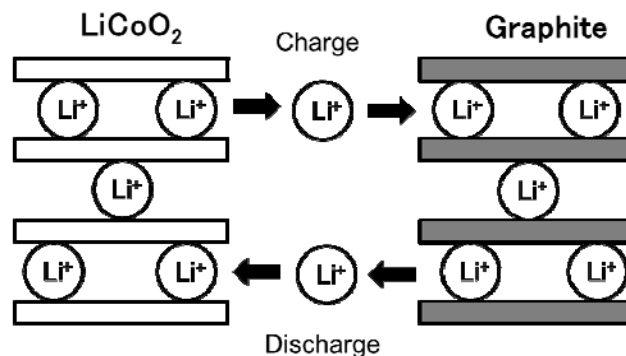


Fig. (2). Battery reactions of a lithium ion battery.

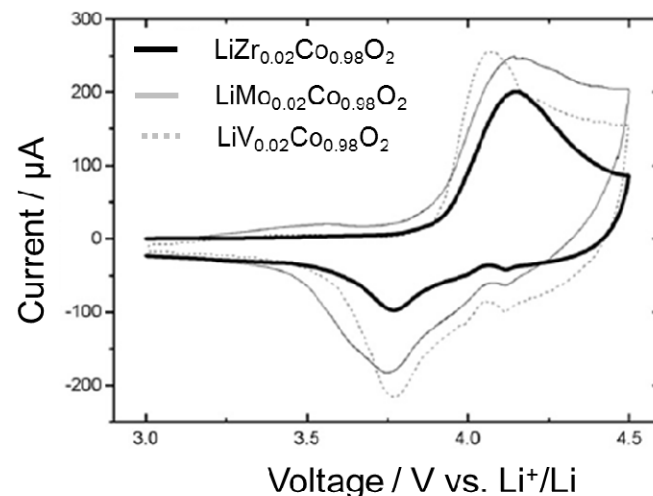


Fig. (3). Cyclic voltammograms of LiCoO_2 substituted by transition metals.

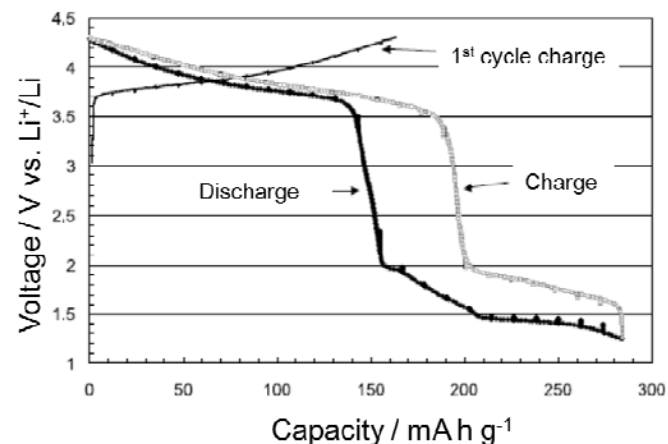


Fig. (4). Charge and discharge curves of $\text{Li}_2\text{Ni}_{0.5}\text{Mn}_{0.5}\text{O}_3$.

However, these higher voltages may cause decomposition of the electrolyte. Thus, this strategy cannot be applied in all cases, as it depends on the nature of the active materials. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ possessing a spinel structure has been previously reported as a cathode material that can charge and discharge stably [17]. In this material, the Ni largely contributes to the charge and discharge reactions, while the Mn keeps its Mn^{4+} state [18]. Fig. (5) shows the charge and discharge curves for $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [19]. Both charge and discharge curves have a plateau of approximately 4.7 V, and the reversibility is also relatively stable. $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ is expected to be a high-energy cathode material if an electrolyte with high resistance towards oxidation can be developed.

Additionally, many cathode materials have been developed to overcome several safety issues. Among these materials, LiMn_2O_4 possessing a spinel structure has been widely reported. Although a critical issue of this material was the dissolution into the electrolyte, this issue was solved by improvement of the crystallinity. Fig. (6) is a SEM image of LiMn_2O_4 with high crystallinity [20]. A single crystal of LiMn_2O_4 , with a size of approximately 100 μm , was obtained through calcination at 900 $^\circ\text{C}$ using LiCl as a flux.

The use of an oxide as a cathode material possesses an intrinsic safety problem because it may release oxygen into the electrolyte, potentially causing a fire hazard. In phosphate and silicate materials, Si and P bond strongly to oxygen atoms. This strong bond can prevent the release of oxygen into the electrolyte [21,22]. Therefore, the use of phosphate and silicate materials as cathodes has been extensively studied. Among them, LiFePO_4 has already succeeded in practical use [23]. Fig. (7) displays TEM images of hydrothermally synthesized LiFePO_4 [24]. It was found that the particle size synthesized was approximately 1 μm with high crystallinity (Fig. 7a). Additionally, a carbon coating was added to the surface of the particles (Fig. 7b). The phosphate and silicate materials are inferior electronic conductors when compared to the oxide materials; therefore, a carbon coating is required to provide electronic conductivity. Several other phosphate and silicate materials such as LiMnPO_4 [25],

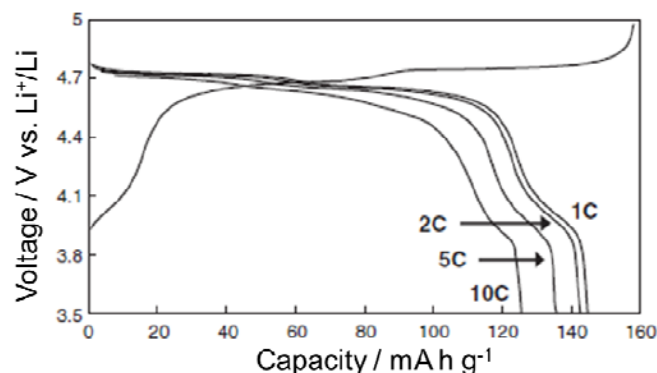


Fig. (5). Charge and discharge curves of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$.

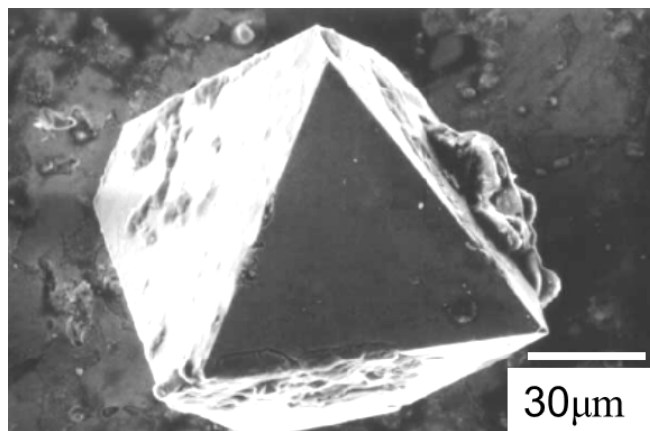


Fig. (6). SEM image of LiMn_2O_4 .

LiNiPO_4 [26], LiCoPO_4 [27], and $\text{Li}_2\text{FeSiO}_4$ [28] in addition to LiFePO_4 have been reported. The charge and discharge voltage of LiMnPO_4 is 4.1 V [29], which is higher than that of LiFePO_4 (3.5V), implying that higher energy density can be achieved. For this reason, LiMnPO_4 is a very attractive material, although low Li^+ and electronic conductivities still remain issues to be overcome. Research on silicate materials has just begun, and new findings are to be expected.

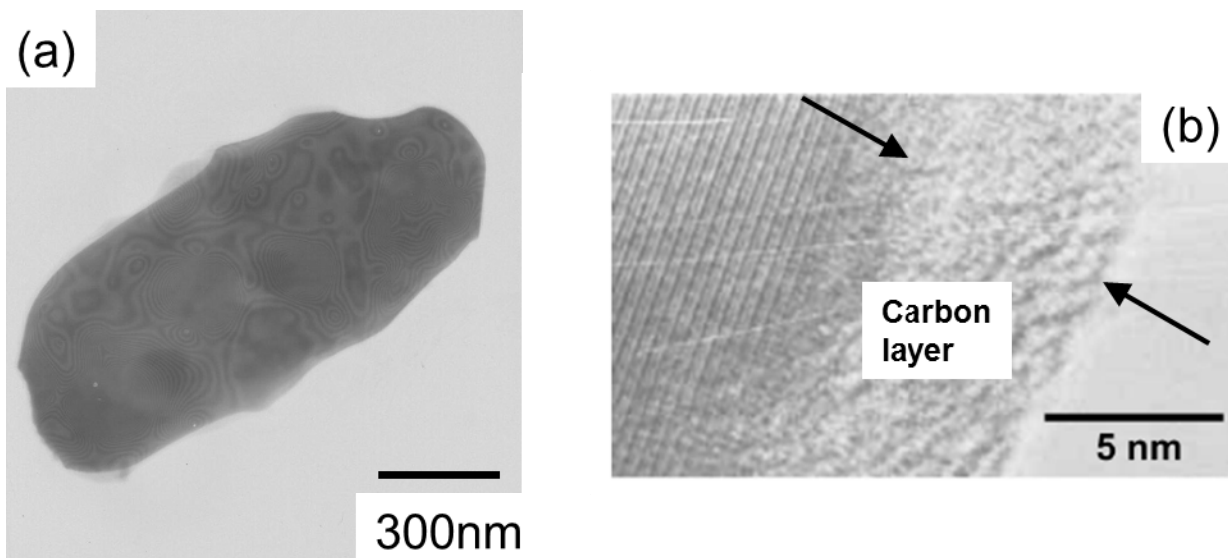


Fig. (7). TEM images of hydrothermally synthesized LiFePO_4 .

3.2. Anode materials

Carboneous materials have been mainly used as anode materials for lithium ion batteries [30]. Although the energy densities of the carboneous materials are very high, the charge and discharge voltages are very close to that of lithium deposition. Thus, lithium deposition could occur by overpotential, especially under a high charge rate, which causes a large polarization [31]. The deposition of lithium metal within the battery causes a serious safety concern, which may lead to an explosion. To overcome this, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ has been developed as an anode material and is already used in practice [32]. The charge and discharge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$ in Fig. (8) show an extremely flat region, and the Li^+ intercalation/deintercalation reaction proceeds around 1.5 V vs. Li^+/Li . This implies that the lithium deposition can be avoided, even under high charge rate [33].

Alternatively, a conversion reaction has been proposed as a viable strategy to increase the capacity of the anode [34]. The conversion reaction is where the metal oxides are reduced to metal and lithium oxide. The capacity is much higher than present carboneous materials and is recognized as one of the promising strategies. To date, CoO , FeO , CuO and others have been tested [35]. The reduction products, metal and lithium oxide, which are high reactivity and low electronic conductivity, respectively, exhibit poor cycle

stability and possess several safety concerns, both of which have not been solved yet.

3.3. Electrolyte

Organic solvents with lithium salts have been used as the electrolyte for lithium ion batteries thus far [36]. This organic electrolyte reveals high Li^+ conductivity and has contributed much towards the high battery performance. However, its flammable nature is a safety concern [37]. Non-flammable solid electrolytes have been thought of as possible candidates to improve the safety of lithium ion batteries. There are two types of solid electrolytes: polymers and ceramics. Among these, ceramic electrolytes are promising in terms of their high Li^+ conductivity and unity transport number [38]. Table 1 shows representative ceramics electrolytes that have been reported so far [39-49]. They primarily consist of oxide, sulfide, phosphate, and silicate ceramics [50]. Previously, when an all-solid-state battery was constructed using oxide, phosphate, and silicate solid electrolytes, a good contact between the solid electrolyte and anode and/or cathode materials could not be readily obtained, providing much difficulty in fabricating an all-solid-state battery. However, a sulfide solid electrolyte can easily make a good electrolyte/electrode contact, implying that the fabrication of all-solid-state battery using a sulfide electrolyte can be achieved

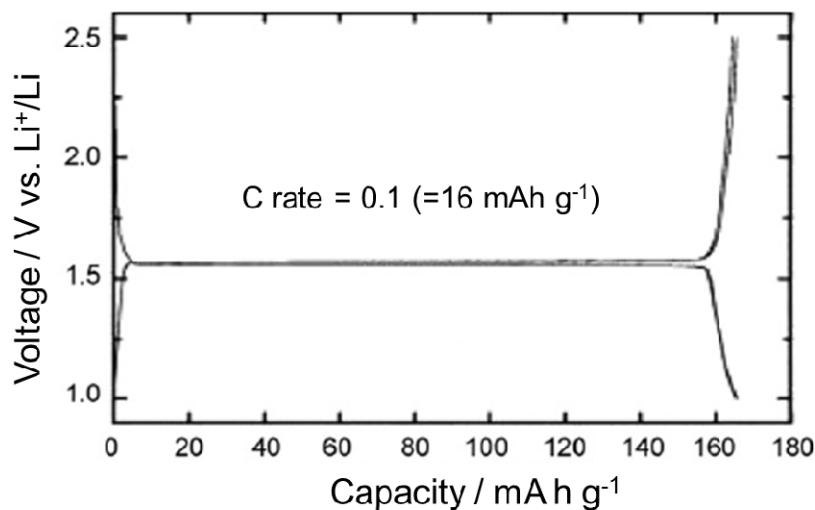


Fig. (8). Charge and discharge curves of $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

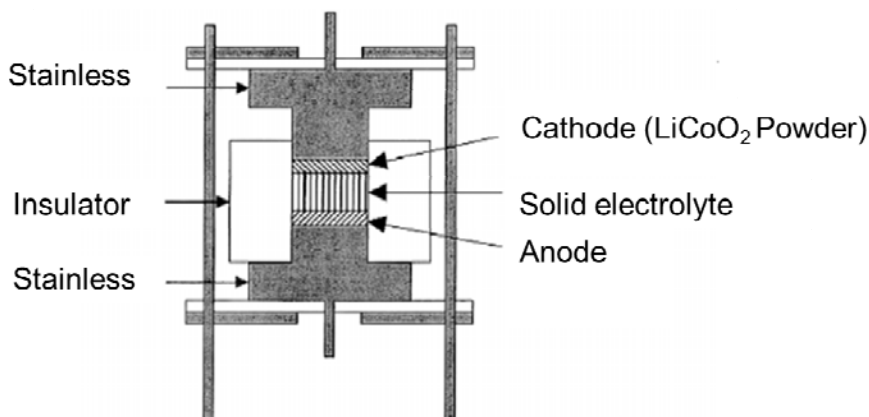


Fig. (9). Schematic illustration of an all-solid-state battery with a sulfide solid electrolyte.

without major issues. Fig. (9) shows a schematic illustration of an all-solid-state battery composed of sulfide solid electrolyte powder, cathode material powder, and Li metal anode [51]. The sulfide solid electrolyte is not reduced by contact with Li metal, and accordingly, the all-solid-state battery with Li metal anode can be constructed when the sulfide solid electrolyte is used. The charge and discharge curves of the battery are depicted in Fig. (10) [52]. Its performance was relatively high, comparable to that of Li battery using a liquid electrolyte. In the case of the oxide solid electrolyte, this configuration causes high impedance and is the largest shortcoming of the oxide solid electrolyte. To overcome this shortcoming, a porous solid electrolyte, which has active material in the pore, has been proposed [53]. Fig. (11) displays SEM images of a solid electrolyte with a three dimensionally ordered structure (3DOM) (Fig. 11a) as well as a solid electrolyte after the loading of active material (Fig. 11b) [54]. This structure can then cause a large area of solid electrolyte/solid active material contact and thus reduce the cell impedance. Fig. (12) depicts a Nyquist plot of the all-solid state battery with 3DOM $\text{Li}_{1.5}\text{Al}_{0.5}\text{Ti}_{1.5}(\text{PO}_4)_3$ (LATP) filled with $\text{Li}_4\text{Mn}_5\text{O}_{12}$. Li metal was used as the anode. The

impedance was dramatically reduced using the 3DOM solid electrolyte. As aforementioned, some modifications are needed to fabricate an all-solid-state battery.

4. APPLICATIONS FOR ELECTRIC VEHICLES

The lithium battery has been expected as a power source for electric vehicle (EV) [55]. Assuming that an EV can drive approximately 500 km on a single charge, the battery should have an energy density of $500 \sim 700 \text{ kW h kg}^{-1}$. If the battery operates at 4V, it would have a required capacity of $125 \sim 175 \text{ A h kg}^{-1}$. However, the battery contains packaging and other materials that do not participate in battery reaction. Approximately 60% of the total weight of the battery is occupied by active material. Thus, the battery for the EV is required to have a capacity of $208 \sim 292 \text{ A h kg}^{-1}$. Such high capacities cannot be achieved through present battery systems. One of the promising batteries using a solid electrolyte, which would be able to meet the high capacity requirements, is shown in Fig. (13). In this battery, the anode and cathode face each other three dimensionally, and the thickness of the solid electrolyte is reduced to below $10 \mu\text{m}$, which allows for

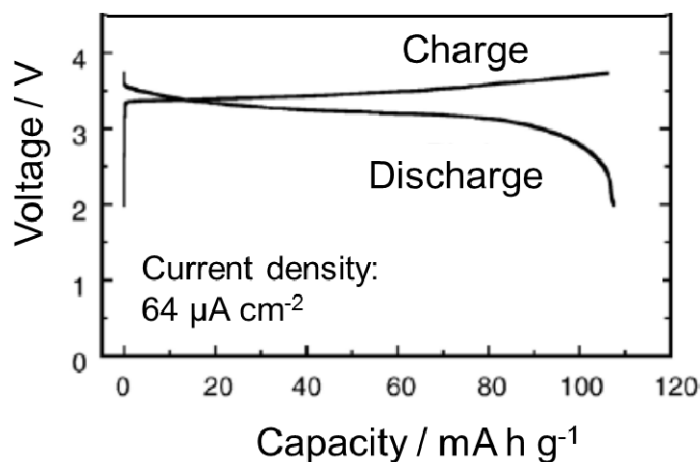


Fig. (10). Charge and discharge curves of an all-solid-state battery with a sulfide solid electrolyte.

Table 1. Li^+ Conductive Ceramics

Electrolyte	Conductivity (S/cm)	Reference
$\text{Li}_2\text{S-P}_2\text{S}_5$	2.1×10^{-3}	[39]
$70\text{Li}_2\text{S} \quad 27\text{P-S}_5 \quad 3\text{P}_2\text{O}_5$	3.0×10^{-3}	[40]
Li_3N	6×10^{-3}	[41]
$\text{Li}_{4.3}\text{Al}_{0.3}\text{Si}_{0.7}\text{O}_4$	6.7×10^{-4} (100°C)	[42]
$\text{Li}_{0.35}\text{La}_{0.55}\text{TiO}_3$ (LLT)	1.4×10^{-4}	[43]
$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ)	4.7×10^{-4}	[44]
$\text{Li}_{2.9}\text{PO}_{3.3}\text{N}_{0.46}$	2.3×10^{-6} (25°C)	[45]
$\text{Li}_9\text{SiAlO}_8$	2.3×10^{-7} (25°C)	[46]
$\text{LiZr}_2(\text{PO}_4)_3$	7×10^{-4} (300°C)	[47]
$\text{Li}_5\text{La}_3\text{Ta}_2\text{O}_{12}$, $\text{Li}_5\text{La}_3\text{Nb}_2\text{O}_{12}$	$\sim 10^{-6}$ (25°C)	[48]
$\text{Li}_6\text{BaLa}_2\text{Ta}_2\text{O}_{12}$	4×10^{-5} (22°C)	[49]

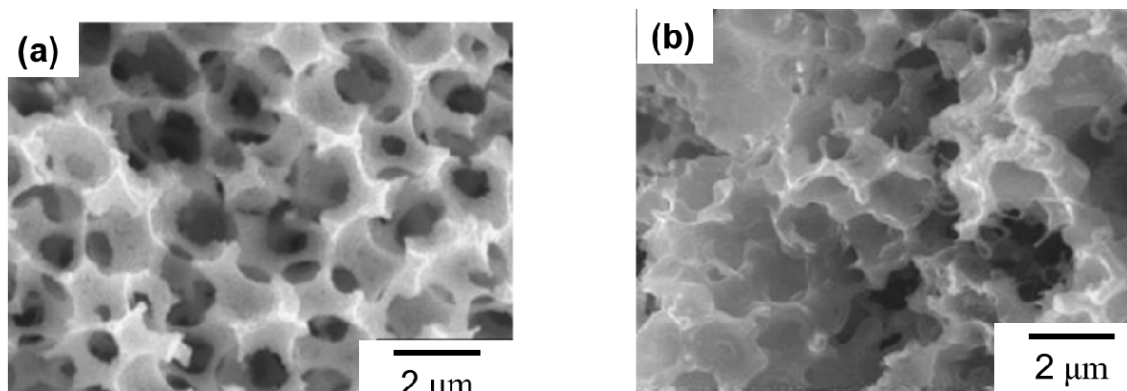


Fig. (11). SEM images of 3DOM solid electrolyte, (a) 3DOM solid electrolyte and (b) after filling with active material.

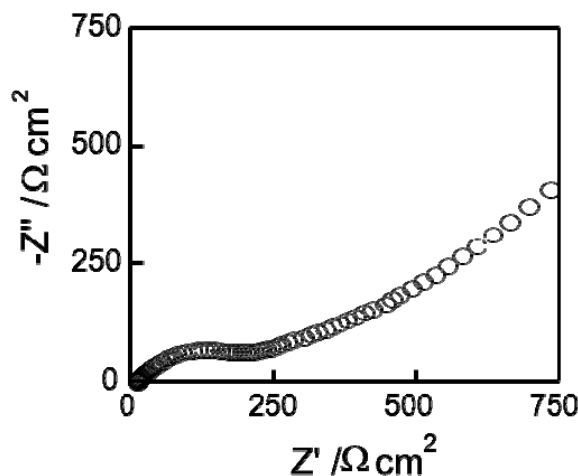


Fig. (12). A Nyquist plot of $\text{Li}_4\text{Mn}_5\text{O}_{12} / 3\text{DOM LATP}$.

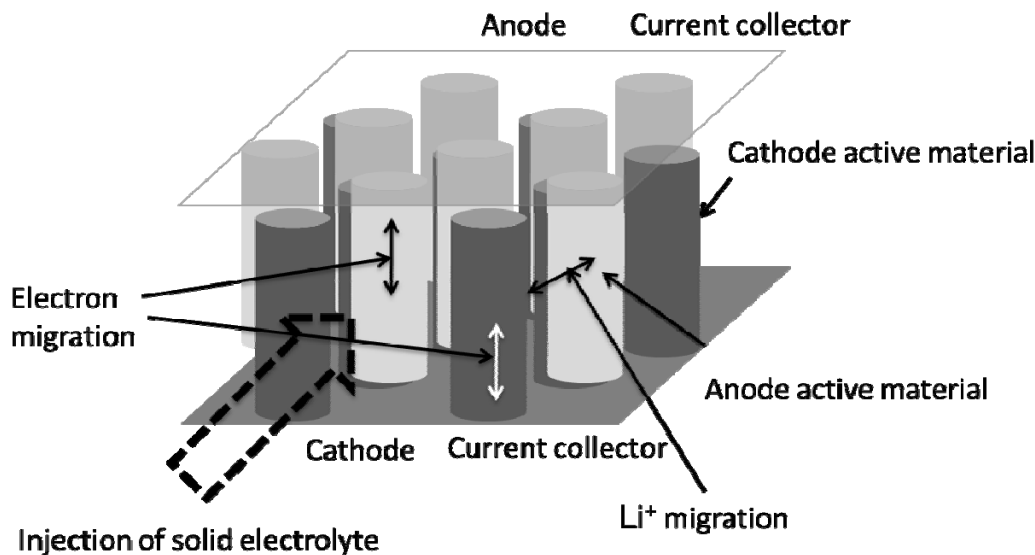


Fig. (13). Proposed structure of a high-performance all-solid-state battery.

the fast migration of Li^+ ions. Currently, the processing techniques needed to prepare such a battery have not been developed yet.

5. SUMMARY

Recent researches of cathode, anode and electrolyte materials are described. For electric vehicle application, im-

provement of energy and power densities and safety are needed. The all-solid-state lithium battery is one of the promising batteries to match the requirement. Therefore, the development of ceramic materials, which comprise anode, cathode and electrolyte, will become increasingly important within the lithium battery industry. As described above, not only properties of anode, cathode and electrolyte materials,

but also a configuration of the all-solid-state battery is very important. Consequently, research on the techniques to form and process the ceramic materials will become a key for the all-solid-state battery development. In order to develop the lithium battery for the electric vehicle, both researches on material and process techniques are strongly required.

CONFLICT OF INTEREST

None declared.

ACKNOWLEDGEMENTS

None declared.

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