

A Study on Electrode Design for Improving the Energy Density of All-Solid-State Batteries- Anode with in-situ Formed Electrolyte

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**A Study on Electrode Design for Improving the
Energy Density of All-Solid-State Batteries- Anode
with *in-situ* Formed Electrolyte**

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Chapter 1

Introduction

1.1 Research Background

Lithium-ion batteries (LIBs) have emerged as a pivotal technology in modern energy storage systems, finding applications in various fields ranging from portable electronic devices to electric vehicles (EVs) and grid-scale energy storage.^[1] Over the past few decades, LIBs have revolutionized the landscape of rechargeable energy storage due to their high energy density and efficiency, long cycle life, and relatively low self-discharge rate compared to other battery technologies.^[2,3] These advantages have fueled their widespread adoption and made them central to the transition toward more sustainable energy systems.

Despite their successes, lithium-ion batteries face several critical challenges. One of the primary limitations is the energy density of current LIBs, while superior to many alternatives, still falls short of the demands for longer-range EVs and higher-capacity grid storage.^[4] For safety concerns, including the risk of thermal runaway and flammability, further underscore

the need for continuous improvement in battery design and materials.^[5]

Current research efforts are focused on addressing these challenges through several key strategies. First, there is an ongoing push to develop alternative active materials and optimize existing materials for electrode. Silicon-based anode, for example, promise significantly higher theoretical capacities than conventional graphite anodes.^[6] In the meanwhile, enhance the performance of cathode materials such as LiFePO_4 (LFP) or $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$ (NCM) to offer potential benefits in terms of safety and energy density.^[7-9] Second, all-solid-state batteries which use solid electrolytes are being explored to replace conventional Li-ion batteries with liquid electrolyte, because solid electrolytes could mitigate safety risks and improve energy density.^[10]

In summary, lithium-ion battery technology sits at the crossroads of critical energy and environmental challenges. While substantial progress has been made, further advancements in materials, safety, performance, and recycling are necessary to fully realize the potential of this technology in supporting the global shift toward renewable energy and electrification. This research aims to contribute to these efforts by exploring advanced anode materials for all-solid-state batteries and novel anode construction to enhance the performance and sustainability of lithium-ion batteries.

1.2 Li-ion Batteries (LIBs)

1.2.1 Discover and History of LIBs

Lithium-ion batteries (LIBs) are a popular type of rechargeable battery widely used in various applications, from consumer electronics to electric vehicles and energy storage. The idea of using metallic lithium as anode due to its most electrochemical negativity (-3.04 V vs standard hydrogen electrode), which make it an excellent candidate for energy storage. In 1976, Stanley Whittingham developed the first lithium-based battery, using titanium disulfide (TiS_2) as the cathode and metallic lithium as the anode. However, due to issues with safety—mainly caused by lithium dendrite formation leading to potential short circuits—this early design was deemed unsafe for commercialization.^[11]

A significant breakthrough came in 1980 when John B. Goodenough discovered that lithium cobalt oxide (LiCoO_2) could be used as a cathode material, allowing for better stability and higher energy density.^[12] This discovery, combined with Akira Yoshino's development of a carbon-based anode (rather than metallic lithium), resulted in the first commercially viable lithium-ion battery, released by Sony and Asahi Kasei in 1991. This combination of materials led to a safer, more efficient rechargeable battery, paving the way for widespread use.^[1]

1.2.2 Construction of LIBs

Commercial LIBs are primarily composed of five key components: the current collector, anode, cathode, electrolyte, and separator (Fig. 1-1). Table 1-1 exhibits the primary materials of LIBs. The current collector serves as a support for the anode and cathode materials and facilitates the collection and distribution of electrical current generated by active materials during charge and discharge processes. It requires excellent electrical conductivity and stable chemical and electrochemical properties. Copper and aluminum foils are the most commonly used current collectors. Due to the high potential at the cathode, aluminum foil, with a relatively high oxidation potential, is used as the current collector. On the anode side, however, aluminum tends to react with lithium ions to form lithium-aluminum compounds, leading to corrosion; thus, copper foil is typically used as the anode current collector.^[13]

The anode and cathode are the main components responsible for energy storage and release in a LIB. The electrode where oxidation occurs is called the cathode, while the electrode where reduction takes place is called the anode. In commercial LIBs with liquid electrolyte, the anode and cathode generally include not only the active materials that participate in electrochemical reactions but also conductive agents and binders to enhance performance. Currently, graphite, silicon, and lithium titanate oxide

($\text{Li}_4\text{Ti}_5\text{O}_{12}$: LTO) are popular anode materials, while lithium cobalt oxide (LiCoO_2 : LCO), lithium iron phosphate (LiFePO_4 : LFP), and nickel cobalt manganese oxide ($\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$: NCM) are widely used cathode materials.^[14]

The electrolyte facilitates lithium-ion transport between the anode and cathode, directly influencing the battery's conductivity, capacity, and output voltage. Typically, the electrolyte consists of a lithium salt, such as lithium hexafluorophosphate (LiPF_6), dissolved in organic solvents like ethylene carbonate (EC), ethyl methyl carbonate (EMC) and dimethyl carbonate (DMC).^[15]

The separator, a thin, microporous membrane, is positioned between the cathode and anode. Its role is to prevent direct contact between the electrodes, thus avoiding short circuits, while allowing ion transport. Polyethylene (PE) and polypropylene (PP) are the primary materials used in commercial separators.^[16]

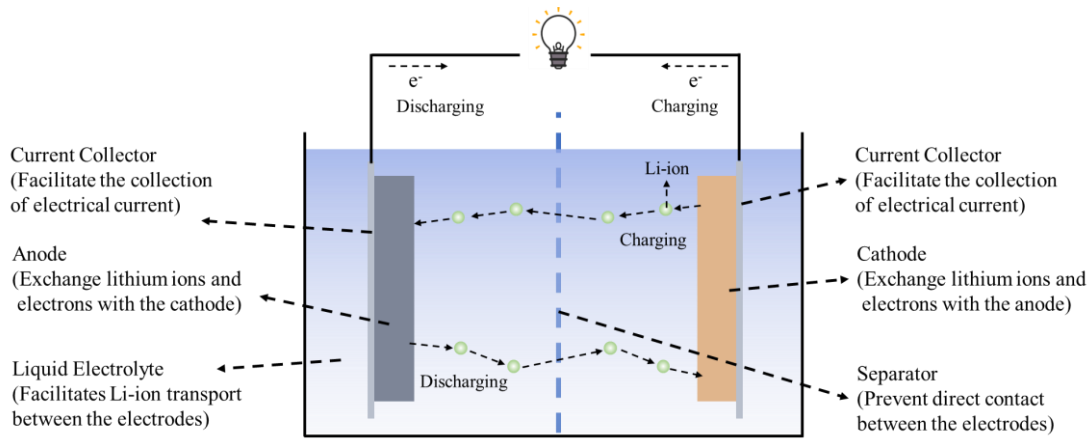


Figure 1-1. Construction of typical liquid LIB.

Table 1-1. List of primary material for liquid LIB.

Component	Primary material
Current Collector	Al foil (Cathode side), Cu foil (Anode side)
Cathode active material	$LiCoO_2$, $LiFePO_4$, $LiNi_xMn_yCo_{1-x-y}O_2$
Anode active material	Graphite, Silicon, $Li_4Ti_5O_{12}$
Binder	PVdF (Polyvinylidene difluoride), PTFE (Polytertrafluoroethylene)
Liquid electrolyte solvent	EC (Ethylene carbonate), EMC (Ethyl Methyl carbonate) DMC (Dimethyl carbonate)
Liquid electrolyte salt	$LiPF_6$
Separator	PE (Polyethylene), PP (Polypropylene)

1.2.3 Working Mechanism of LIBs

LIBs rely on the movement of lithium ions within the cell to create an electric current, enabling the storage and release of electrical energy. During charging, lithium ions migrate from the positive electrode (cathode) to the negative electrode (anode). The cathode, with a high potential and strong oxidation capability, undergoes oxidation, while the anode, with a low potential and strong reduction capability, undergoes reduction. However,

because the electrode reactions during charging are not spontaneous, an external power source is required to apply voltage and drive the reactions.

During discharge, lithium ions move from the anode back to the cathode. The cathode undergoes a reduction reaction, and the anode undergoes an oxidation reaction. These reactions are spontaneous and only require an external load to complete the circuit.

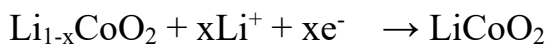
Commercial LIBs generally use electrode material based on intercalation reaction. Taking a battery with LiCoO_2 as the cathode and graphite as the anode as an example (the schematic diagram of charging and discharging process are shown in Fig. 1-2), the reactions are as follows:

Cathode reaction:

Charging:

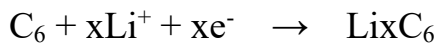


Discharging:

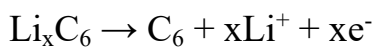


Anode reaction:

Charging:

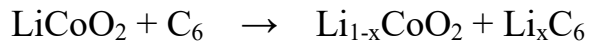


Discharging:



Overall reaction:

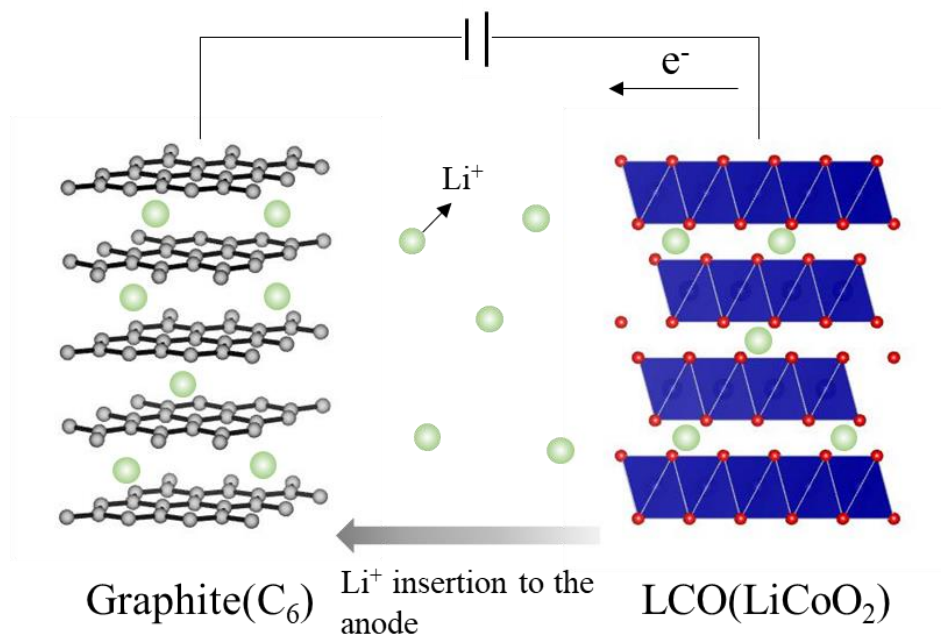
Charging:



Discharging:



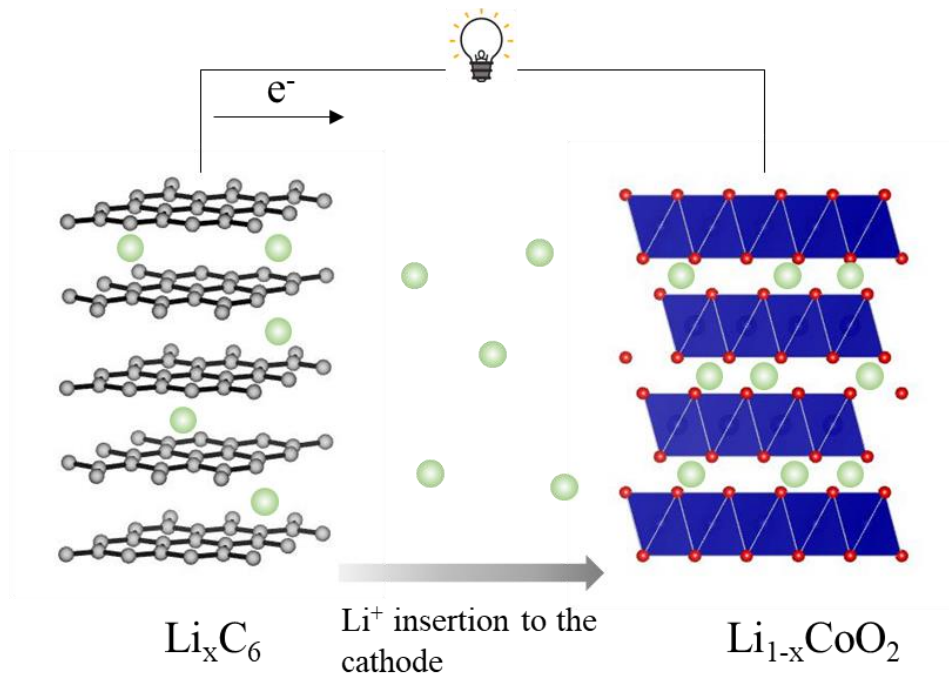
Charging Reaction



Cathode: $\text{LiCoO}_2 \rightarrow \text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + xe^-$ (Oxidation reaction)

Anode: $\text{C}_6 + x\text{Li}^+ + xe^- \rightarrow \text{Li}_x\text{C}_6$ (Reduction reaction)

Discharging Reaction



Cathode: $\text{Li}_{1-x}\text{CoO}_2 + x\text{Li}^+ + x\text{e}^- \rightarrow \text{LiCoO}_2$ (Reduction reaction)

Anode: $\text{Li}_x\text{C}_6 \rightarrow \text{C}_6 + x\text{Li}^+ + x\text{e}^-$ (Oxidation reaction)

Figure 1-2. Schematic diagram of charging and discharging mechanism of LIB.

1.2.4 Electrode active materials for LIBs

Table 1-2 (Properties of typical materials of different reaction types.) and Fig. 1-3 (Schematic diagram of reaction mechanism of (a) intercalation type, (b) conversion type and (c) alloy type.) are exhibited below.

1.2.4.1 Intercalation-type Active Materials

As mentioned above, the current Li-ion batteries mostly utilized active

materials based on intercalation reaction. Which involve the reversible insertion of ions, often lithium ions (Li^+), into the layered structure of certain host materials without significantly changing their crystalline framework. This process is essential in energy storage devices, especially in lithium-ion batteries (LIBs), where it plays a crucial role in both the charging and discharging phases.

In a typical intercalation reaction, during battery charging, lithium ions are extracted from the positive electrode (cathode) and move through the electrolyte to the negative electrode (anode). During discharging, the reverse occurs, with lithium ions moving back to the cathode while releasing electrical energy.

Common intercalation-type active materials in lithium-ion batteries include:

Cathode Materials:

Lithium Cobalt Oxide (LiCoO_2): Offers high energy density and is widely used in consumer electronics.^[12]

Lithium Nickel Manganese Cobalt Oxide (NMC: $\text{LiNi}_x\text{Mn}_y\text{Co}_{1-x-y}\text{O}_2$): A safer option with high energy density, commonly used in electric vehicles.^[8]

Lithium Iron Phosphate (LiFePO_4): Known for its thermal stability and long cycle life, often used in applications requiring high safety such as electric vehicles.^[7]

Anode Materials:

Graphite (C_6): A widely used intercalation material with high lithium-ion storage capacity and stability.^[17]

For intercalation-type active materials, although Li-ions are primarily inserted and deintercalated between the layers of the active material during charging and discharging without affecting the crystal structure or causing significant volume changes. A higher atomic mass and a limited number of intercalated Li-ions are needed to provide and maintain a stable layered structure. This results in a relatively low theoretical capacity compared to other types of reactions, such as conversion or alloying reactions.

1.2.4.2 Alloy-type Active Materials

Alloy-type LIB's active materials refer to alloys that can react with lithium during battery charge and discharge cycles. These materials undergo a reversible alloying and dealloying process with lithium ions, storing and releasing lithium ions through this mechanism. Alloy-type materials often have higher specific capacities compared to traditional intercalation-type active materials, making them promise for high-capacity LIBs.

Some common examples include silicon (Si), tin (Sn), and antimony (Sb), which can form lithium alloys (e.g., Li-Si, Li-Sn) that store a significant amount of lithium.^[18–20] In these cases, Silicon (Si) anodes are highly

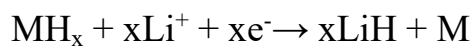
promising in LIBs due to their exceptionally high theoretical specific capacity of around 4198 mAh/g (based on the formation of $\text{Li}_{4.4}\text{Si}$). This capacity far exceeds that of conventional graphite anodes, which offer only about 372 mAh/g.^[21,22]

However, these materials often face challenges such as large volume changes during cycling, which can lead to structural degradation and capacity loss. Research is ongoing to improve the performance and stability of alloy-type lithium battery active materials by using nano-structuring, graphene composites, and binders to mitigate these issues.^[22,23]

1.2.4.3 Conversion-type Active Materials

Conversion-type lithium battery active materials are a class of electrode materials that store and release lithium ions through a conversion reaction, rather than traditional intercalation. In these reactions, a compound (typically a metal oxide (CoO), hydride (MgH_2), or fluoride (FeF_2)) reacts with lithium ions and electrons, undergoing a complete transformation into metallic particle and Li salt.^[24–28]

For example, in transition metal hydrides (e.g., MgH_2 , TiH_2), the reaction can be represented as:



Here, the metal hydride (MH_x) is reduced to form metallic particles (M:

electron conductor) dispersed in a lithium hydride (LiH: Li⁺ conductor) matrix. The reverse process occurs during delithiation, where lithium ions leave the electrode, and the metal returns to its original state.

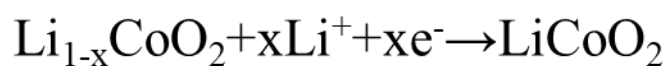
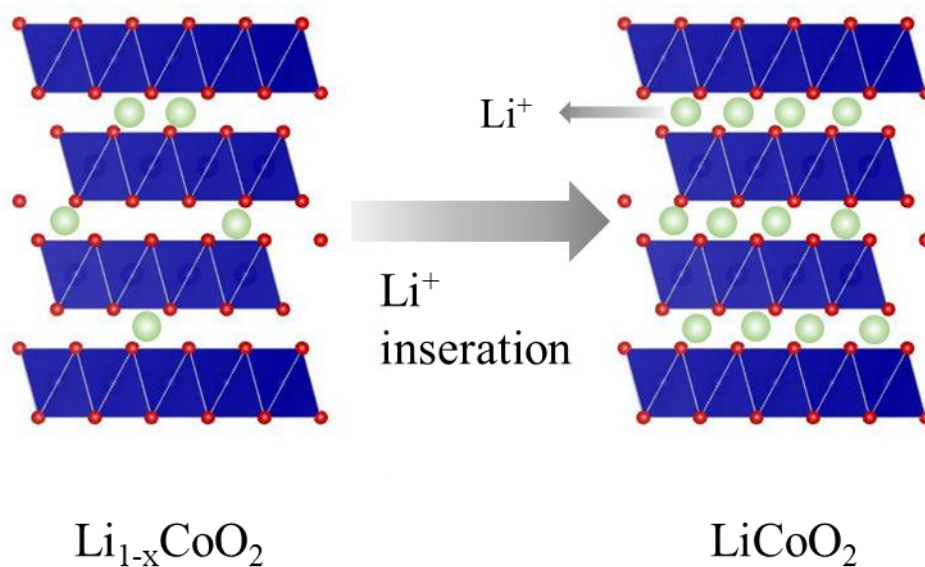
One of the key advantages of conversion-type materials is their high theoretical capacity. Unlike intercalation materials, where lithium ions are inserted into pre-existing layers, conversion-type materials can theoretically store more lithium ions due to the formation of new phases and the larger number of electrons involved in the reaction. For example, MgH₂ has a theoretical capacity of about 2036 mAh/g, much higher than that of graphite (372 mAh/g).^[14,26]

Indeed, while conversion-type active materials offer high theoretical capacities, their volume changes during cycling remain a critical challenge. However, the volume expansion associated with conversion-type materials is generally much smaller compared to that seen in alloy-type materials. This is an important distinction because, although alloy-type materials like silicon undergo drastic volume changes (Si: 420%),^[21] conversion-type materials typically experience more moderate volume fluctuations during the conversion reaction, often in the range of 200-300%. In other words, conversion-type materials tend to offer a better balance between capacity, cycle life, and structural stability.

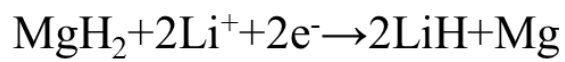
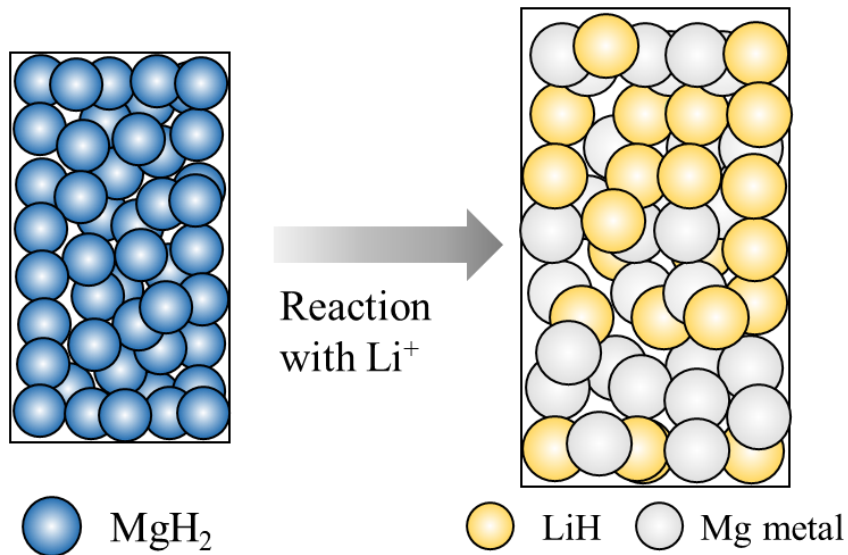
Table 1-2. Properties of typical materials of different reaction types.

Reaction type	Theoretical capacity	Volume expansion
Intercalation reaction(LiCoO_2) ^[12]	274 mAh/g	105-110%
Conversion reaction(MgH_2)	2036 mAh/g	223%
Alloy reaction(Si) ^[21]	4198 mAh/g	420%

a Intercalation reaction



b Conversion reaction



c Alloy reaction

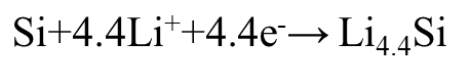
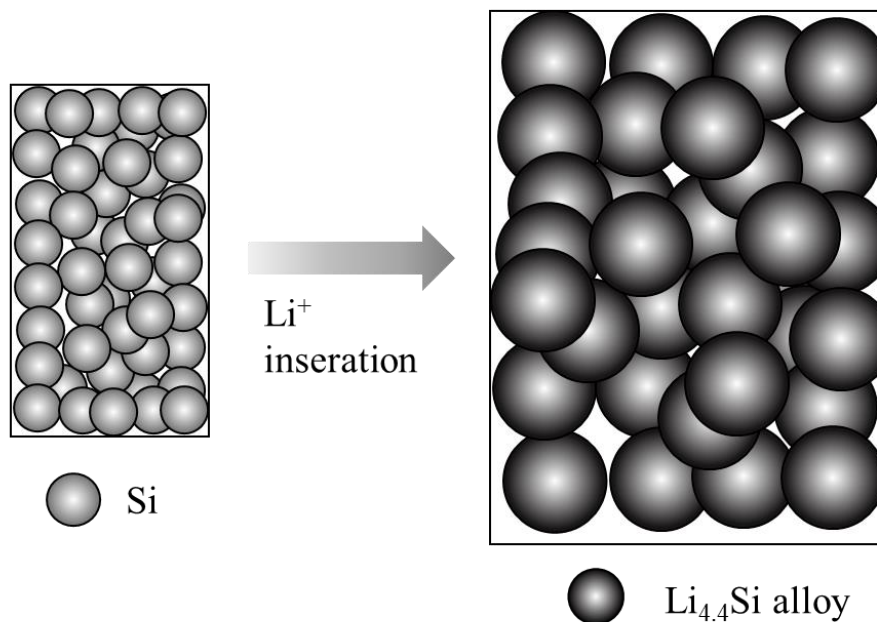


Figure 1-3. Schematic diagram of reaction mechanism of (a) intercalation type, (b) conversion type and (c) alloy type.

1.3 All-solid-state Batteries (ASSBs)

1.3.1 Overview of ASSBs

All-Solid-state batteries are an advanced energy storage technology that replaces the liquid electrolyte used in conventional LIBs with a solid electrolyte. The construction using solid electrolyte (Fig. 1-4) offers a range of benefits, such as high safety, high energy density and low cost of production (ideal situation). These benefits make it a promising candidate for applications in electric vehicles (EVs), consumer electronics, and renewable energy storage.^[29–31] The core components of solid-state batteries include a solid electrolyte, which can be made of ceramic, sulfide, or polymer materials; a cathode, typically similar to those used in traditional batteries; and an anode, often made of metallic lithium or material with high theoretical capacity for its high energy density.^[32]

The inflammable solid electrolyte provides significantly enhanced safety by eliminating flammable organic liquids, reducing risks of leakage, fire, or explosion. Solid electrolytes are also more stable and safer under extreme operating conditions such as overcharging or high temperatures. In high-temperature environments (e.g., 100°C), liquid lithium-ion batteries may experience thermal decomposition and evaporation of the electrolyte (LiPF₆), rendering the battery inoperable. However, the high operating temperature

enhances the ionic conductivity of solid electrolytes, further improving the battery's performance. Another critical advantage of solid electrolytes is hoped to suppress the growth of lithium dendrites to some extent. In traditional liquid electrolyte systems, lithium dendrites—needle-like structures that form during charging—can pierce the separator, causing short circuits. Short circuits will cause increased battery temperature, when the temperature rises, lithium reacts exothermically with the electrolyte, which can lead to thermal runaway. Compared to liquid electrolytes, solid electrolytes particularly exhibit higher mechanical strength and have a certain ability to physically blocks dendrite growth.^[10,33] As a result, solid-state batteries achieve greater safety and reliability compared to liquid-batteries.

In addition to safety, the use of a solid electrolyte allows for bipolar

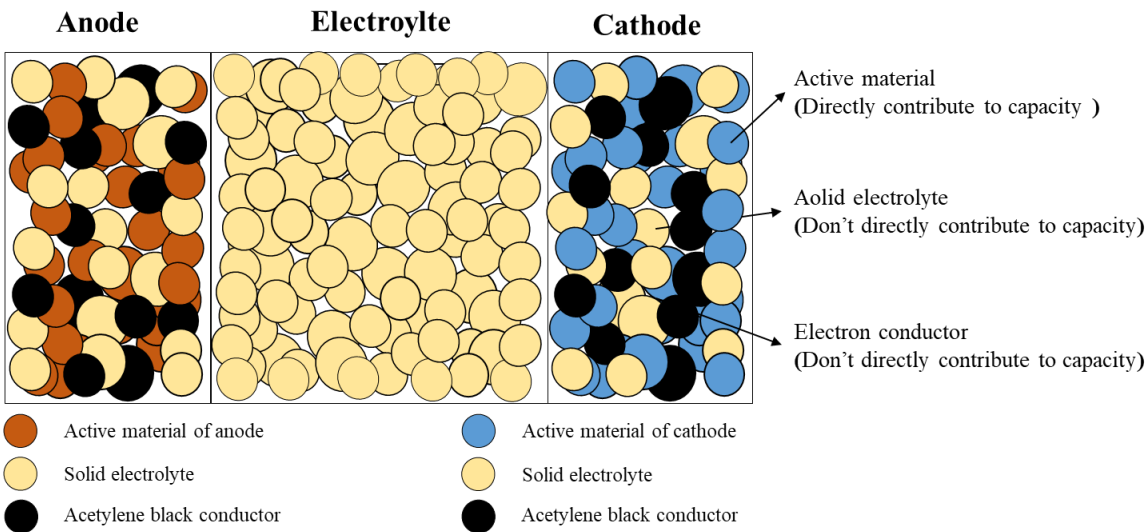


Figure 1-4. Construction of ASSBs.

structure design that further increase energy density. The main reason is the ability to use a single battery pack to contain multiple cells (with a pair of anode and cathode). In conventional lithium-ion designs, if multiple cells are placed in one pack, the electrode reaction will only occur between anode and cathode on both sides of the pack due to liquid junction. Therefore, each cell requires its own separator and liquid electrolyte in a single pack, which increases weight and volume. For all-solid-state batteries, Li-ion can only translate through the solid electrolyte sandwiched by each pair of electrodes, every electrodes can react entirely during charge and discharge process.^[34] By sharing the battery pack, solid-state batteries can achieve a more compact and efficient configuration, reducing redundant components. This structural optimization contributes to a higher volumetric energy density, allowing more energy to be stored in a given space. Schematic diagram of liquid junction and bipolar structure are given in Fig. 1-5.

All-solid-state batteries also face a series of technical and engineering challenges during research and commercialization, primarily involving solid electrolyte material performance and preparation, electrode-electrolyte interface issues, and limitations in active material loading.

Compared to liquid electrolytes, solid electrolytes typically have lower ionic conductivity, especially at room temperature, making it difficult to

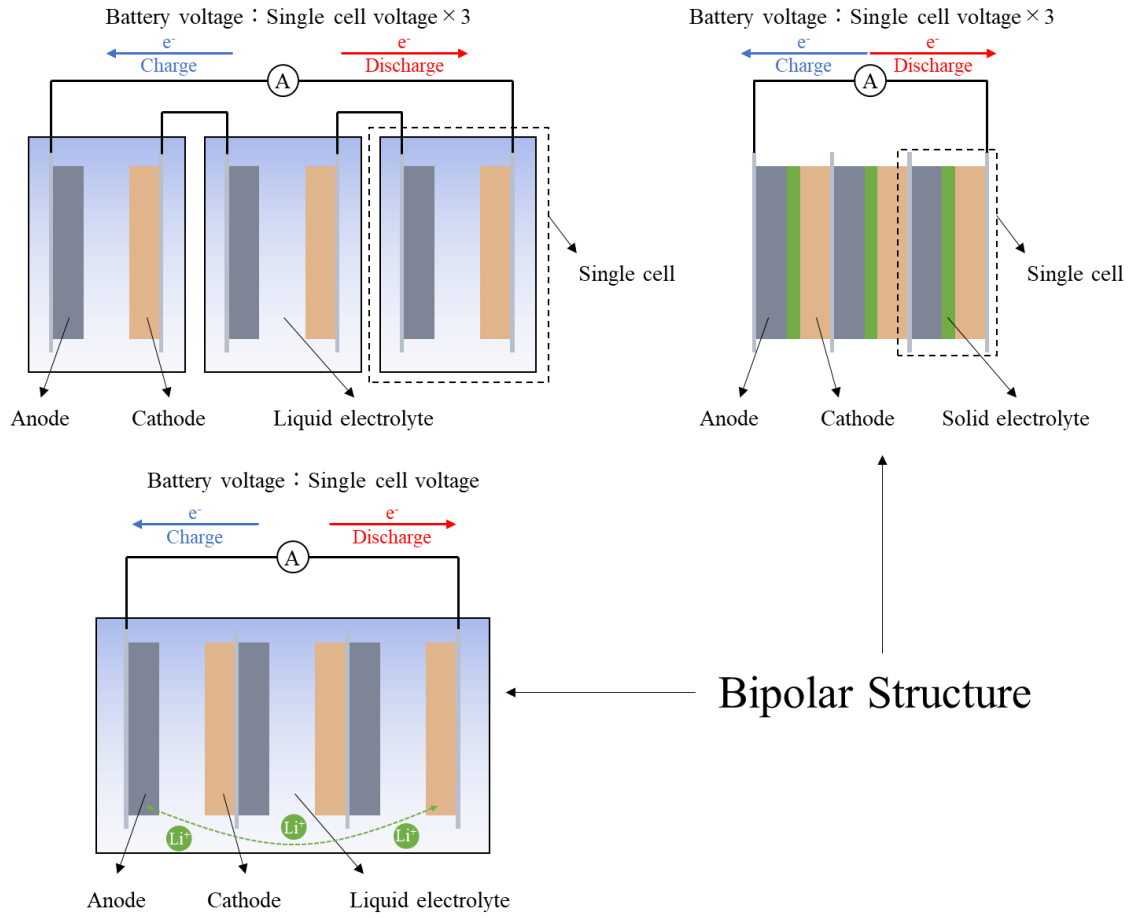


Figure 1-5. Schematic diagram of liquid junction and bipolar structure.

meet rapid charging and discharging requirements. While some materials (such as sulfide electrolytes) have approached liquid electrolyte levels,^[35,36] they still react with air and moisture to generate harmful gases like H_2S , necessitating further optimization.^[37] Moreover, since most solid electrolytes are air-sensitive, their production requires an inert atmosphere, resulting in high manufacturing costs and challenges in large-scale production. Beyond the inherently low conductivity of solid electrolytes, the interface between solid electrolytes and electrodes represents another significant challenge.^[38]

For liquid batteries, liquid electrolytes can permeate and wet electrode surfaces, forming a relatively continuous contact interface. This contact mode helps reduce interface impedance and enhance ion conduction efficiency. However, solid electrolyte-electrode contact relies on mechanical pressure and surface planarity. Since solids cannot flow like liquids, interfaces cannot fully conform, potentially creating micropores and gaps that increase interface impedance and reduce ion transport efficiency.

Regarding interface stability, while liquid electrolytes may be more prone to electrode chemical reactions in some cases (such as solvent decomposition or side reactions), the formation of a solid electrolyte interphase (SEI) can partially protect the electrode and inhibit further reactions.^[39] Solid electrolytes similarly react with electrodes, but unlike liquid electrolytes, they cannot self-repair after reaction, leading to interface aging, cracking, or increased impedance. Therefore, solid-state batteries require further improvement of interface performance through material design and interface engineering.

Compared to liquid batteries, the active material loading in solid-state battery electrodes is also constrained by different ion conduction mechanisms. In liquid batteries, electrodes do not need excessive ion-conducting additives because liquid electrolytes can penetrate electrode surfaces and internal structures, providing ion conduction pathways. In

contrast, solid electrolytes cannot diffuse into electrode interiors like liquid electrolytes. Consequently, to ensure sufficient ion diffusibility within electrodes, active materials must be mixed with solid electrolytes during electrode preparation. This approach reduces active material loading, resulting in lower energy density compared to liquid batteries.

1.3.2 Solid Electrolytes

1.3.2.1 Sulfide-based Solid Electrolytes

Among the various solid electrolytes, sulfide-based electrolytes exhibit the highest ionic conductivity. Additionally, due to their relatively low Young's modulus, sulfide electrolytes can be fabricated using cold pressing at room temperature. When sintered at an appropriate temperature after cold pressing, the ionic conductivity can be further enhanced. Sulfide solid electrolytes are primarily composed of sulfur (S), phosphorus (P), and lithium (Li), combined with other elements.

Based on compositional complexity, sulfide electrolytes can be categorized into two main types: binary and ternary sulfide electrolytes. Binary sulfide electrolytes primarily consist of Li_2S and P_2S_5 , with representative materials including Li_3PS_4 and $\text{Li}_7\text{P}_3\text{S}_{11}$.^[40,41] In contrast, ternary sulfide electrolytes incorporate an additional component, MS_2

(where M can be Si, Ge, or Sn), such as $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ (LGPS) and $\text{Li}_6\text{PS}_5\text{X}$ (where X represents Cl, Br, or I).^[42,43] Structurally, these sulfide electrolytes can be further classified into three distinct crystal structure types: thio-LISICON (lithium superionic conductor), tetragonal LGPS, and argyrodite-type $\text{Li}_6\text{PS}_5\text{X}$.^[35]

The thio-LISICON electrolytes, such as $(100-x)\text{Li}_2\text{S}-x\text{P}_2\text{S}_5$, $(100-x)\text{Li}_2\text{S}-x\text{SiS}_2$,^[44] and $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$,^[45] are derived by replacing oxygen in $\gamma\text{-Li}_3\text{PO}_4$ solid electrolytes with sulfur. These materials exhibit ionic conductivities in the range of 10^{-3} to 10^{-4} S/cm at room temperature, significantly outperforming most oxide electrolytes.

A pivotal breakthrough occurred in 2011 when Kanno et al. introduced the $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ electrolyte, featuring a novel 3D framework structure.^[46] Despite sharing elemental composition with previous thio-LISICON materials like $\text{Li}_{4-x}\text{Ge}_{1-x}\text{P}_x\text{S}_4$, this electrolyte presented a unique structural arrangement comprising $(\text{Ge}_{0.5}\text{P}_{0.5})\text{S}_4$ tetrahedrons, PS_4 tetrahedrons, LiS_4 tetrahedrons, and LiS_6 octahedrons. Most notably, $\text{Li}_{10}\text{GeP}_2\text{S}_{12}$ emerged as the first solid electrolyte achieving an unprecedented ionic conductivity of 1.2×10^{-2} S/cm, marking a significant advancement in the field of solid-state electrolyte research.^[35]

$\text{Li}_6\text{PS}_5\text{X}$ (X: Cl, Br, I) system has the same structure with the mineral argyrodite (Ag_8GeS_6) which exhibit a high ionic conductivity of Ag^+ .^[47] In a

series of $\text{Li}_6\text{PS}_5\text{X}$ (X: Cl, Br, I), the $\text{Li}_6\text{PS}_5\text{Cl}$ presented the attractive ionic conductivity of $1.33 \times 10^{-3} \text{ S/cm}$.^[48]

1.3.2.2 Oxide-based Solid Electrolytes

Oxide-based solid electrolytes are characterized by remarkable chemical stability in air and a large potential window. The presence of oxygen contributes to their atmospheric stability at room temperature. However, oxygen's higher electronegativity creates challenges: it generates stronger Li-ion binding energies and constricts ionic migration pathways, thereby constraining Li-ion mobility. To achieve high relative density and enhanced ionic conductivity, these oxide solid electrolytes typically undergo high-temperature sintering processes. Within the broader family of oxide solid electrolytes, only a select few lithium-conducting compounds have demonstrated impressive room-temperature ionic conductivities exceeding 1 mS/cm. These notable materials include LLTO ($\text{Li}_{3.3}\text{La}_{0.56}\text{TiO}_3$), LATP ($\text{Li}_{1.3}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3$), and LLZO ($\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$). Notably, these materials represent the three primary crystal structures found in oxide electrolytes:

LLTO exemplifies the perovskite structure, It typically has the chemical formula ABO_3 , where A and B represent different metal ions, and O is the oxygen ion.^[49]

LATP represents the NASICON structure, the typical chemical formula is

$\text{Li}_3\text{M}_2(\text{XO}_4)_3$ (where M is a transition metal and X is P, S, Si, Mo, W, etc.). The MO_6 octahedra and XO_4 tetrahedra share vertices, and lithium can occupy two distinct sites within the structure. There is a 6-coordinate M1 site directly located between two MO_6 octahedra and an 8-coordinate M2 site located between the columns of the MO_6 octahedra. These two sites enable lithium ions to achieve high ionic conductivity.^[50,51]

LLZO embodies the garnet structure, The general composition is represented as $\text{A}_3\text{B}_2(\text{XO}_4)_3$ (where A = Ca, Mg, La; B = Al, Fe, Ga, Ge, Mn, V; X = Si, Ge, Al). Lithium ions occupy the A or B sites. Due to their high thermal stability and excellent chemical stability with lithium metal, they are attracting attention as promising candidates for oxide-based solid electrolytes.^[52]

In contrast, the performance of oxide electrolytes are limited by high grain boundary resistance or poor physical contact with electrode.^[36]

1.3.2.3 Hydride-based Solid Electrolytes

Hydride-based solid electrolytes are typically represented by the formula LiMH_n , where incorporates a complex anion (MH_n) such as $[\text{BH}_4]^-$, $[\text{NH}_2]^-$, or $[\text{AlH}_4]^-$. Among these, lithium borohydride (LiBH_4) stands out as a notable example, characterized by an ionic bonding arrangement between Li^+ cations and $[\text{BH}_4]^-$ anions.^[53] At room temperature, LiBH_4 crystallizes in

an orthorhombic structure with the space group *Pnma* (low-temperature phase, LT) and exhibits very low ionic conductivity, with values ranging from 10^{-8} to 10^{-6} S/cm. When the material is heated to approximately 390 K, LiBH_4 undergoes a structural phase transition to a hexagonal structure with the space group *P6₃mc* (high-temperature phase, HT). This structural modification results in a dramatic increase in ionic conductivity by three orders of magnitude, reaching approximately 10^{-3} S/cm.^[54,55] In the LT phase, each Li^+ ion is tetrahedrally coordinated by four $[\text{BH}_4]^-$ anions, a configuration that restricts the mobility of Li^+ ions. In contrast, the HT phase features a rearrangement of Li^+ ions along the a and b axes, free from significant hindrance. This structural transformation is believed to facilitate the migration of Li^+ ions along a,b axes, accounting for the enhanced ionic conductivity in the HT phase.^[56] The structure of LT and HT phases are exhibited in Fig. 1-6.

For further applications, the development of hydride electrolytes with high ionic conductivity at low temperatures is also crucial. Currently, two main trends are emerging: one is doping to lower the phase transition temperature of LiBH_4 , and the other is the development of complex electrolytes based on polyanions with larger ionic radius.

The incorporation of lithium halides (LiX), including LiCl , LiBr , and LiI , to LiBH_4 can stabilize the HT phase at low temperature (25°C). For MBH_4

($M = \text{Na, K, Rb, and Cs}$), researchers have observed that increased distances between adjacent $[\text{BH}_4]^-$ correlate with decreased transition temperatures.^[53] Therefore, replacing $[\text{BH}_4]^-$ with I^- , whose ionic radius (0.220 nm) is larger than that of the $[\text{BH}_4]^-$ (0.205 nm), can effectively improve the stability of HT phase. $0.75\text{LiBH}_4\text{-}0.25\text{LiI}$ can exhibit high conductivity of 10^{-4} S/cm at 25°C (conductivity is shown in Fig. 1-7).^[57-59]

Recent studies on improving the ionic conductivity of complex hydrides have highlighted a range of *closo*-type (cage-like) complex hydrides, including $\text{Li}(\text{CB}_9\text{H}_{10})$, $\text{Li}(\text{CB}_{11}\text{H}_{12})$, and $\text{Li}_2(\text{B}_{12}\text{H}_{12})$. Closo-type hydrides possess a natural advantage in ionic conduction over LiBH_4 -based complex hydrides, thanks to their large, polyanionic complex anions. These anions form conduction pathways that promote efficient ionic diffusion while requiring low activation energy.^[60,61] A recent study revealed that partial substitution of the $[\text{CB}_9\text{H}_{10}]^-$ complex anions in $\text{Li}(\text{CB}_9\text{H}_{10})$ with $[\text{CB}_{11}\text{H}_{12}]^-$ anions can achieve $(1-y)\text{Li}(\text{CB}_9\text{H}_{10})\text{-}y\text{Li}(\text{CB}_{11}\text{H}_{12})$ system, which stabilizes a disordered structure at room temperature. This structure closely resembles the high-temperature phase of $\text{Li}(\text{CB}_9\text{H}_{10})$. The stabilized high-temperature phases with $y=0.3$ ($0.7\text{Li}(\text{CB}_9\text{H}_{10})\text{-}0.3\text{Li}(\text{CB}_{11}\text{H}_{12})$) exhibit lithium superionic conductivities exceeding 10^{-3} S/cm at 25°C (conductivity is shown in Fig. 1-8).^[62,63]

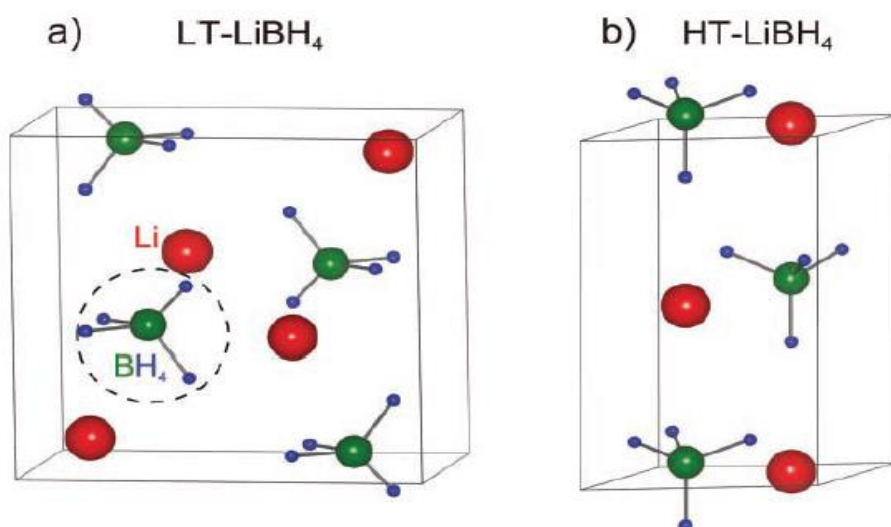


Figure 1-6. Crystal structure of LiBH₄ LT phase (a) and HT phase (b). [53]

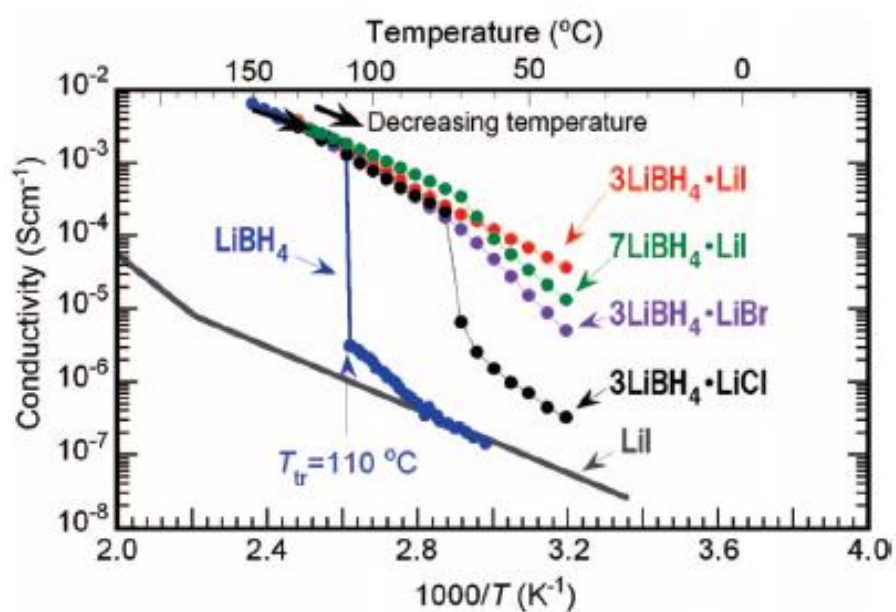


Figure 1-7. Arrhenius plot of LiBH₄, LiI and LiBH₄+LiM(M:I, Br, Cl). [58]

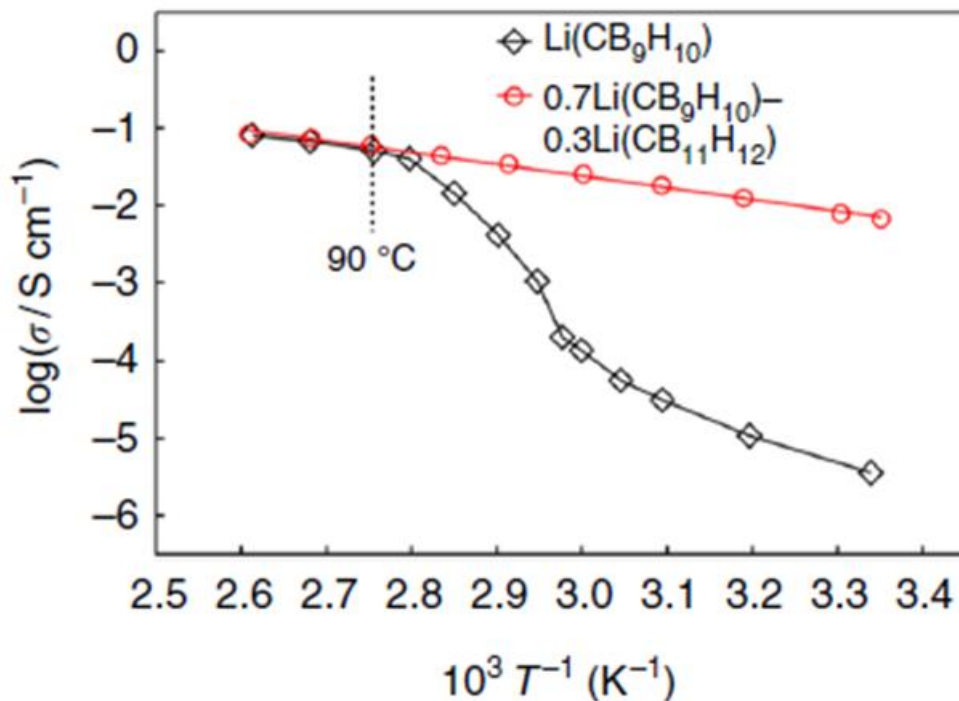


Figure 1-8. Arrhenius plot of $\text{Li}(\text{CB}_9\text{H}_{10})$ and $0.7\text{Li}(\text{CB}_9\text{H}_{10})-0.3\text{Li}(\text{CB}_{11}\text{H}_{12})$. [62]

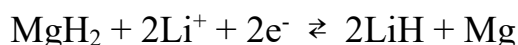
1.4 Metal Hydride Anodes

1.4.1 MgH_2 anode

MgH_2 (magnesium hydride) can be used as an anode material in both liquid and solid-state lithium batteries due to its high theoretical capacity and relatively low potential. The theoretical capacity of MgH_2 is 2036 mAh/g, which is significantly higher than that of graphite (372 mAh/g) used in conventional lithium-ion batteries.^[26] However, MgH_2 is a typical conversion active material, the volume change during the charge-discharge cycle can be as high as 230% due to the formation of Mg and LiH. The redox

potential of MgH_2 as an anode material is around 0.5 V (vs. Li/Li^+), which is higher than the potential of Li dendrite (0 V vs. Li/Li^+), decrease the risk of short circuit. The high theoretical capacity and relative low potential make MgH_2 an attractive candidate for high-energy-density batteries.

MgH_2 was first used as anode material of lithium batteries in 2008.^[64] Its electrode reaction was shown below:



which is a reversible reaction with Li-ion. However, when MgH_2 was used in liquid batteries, the reversibility is extremely poor due to the dissolution of Metallic Mg in the liquid electrolyte and the formation of Li-Mg alloys.^[65] Although the impact of Li-Mg alloys (formed at 0.1V vs Li/Li^+) can be mitigated by adjusting the charge and discharge cutoff voltage, the issue of Metallic Mg dissolution remains difficult to solve, thus restricts the use of MgH_2 in liquid batteries.

Fortunately, if MgH_2 is used in the ASSBs, dissolution of Metallic Mg will disappear, and reversibility can be significantly improved.^[66] In addition, the rapid mobility of H^- also facilitates the electrode reaction of MgH_2 .^[67,68] When LiBH_4 is used as the solid electrolyte, the exchange effect between LiBH_4 and MgH_2 (the exchange of H^-) can further accelerate the electrode reaction kinetics of MgH_2 .^[69] However, there are still some challenges that need to be overcome with MgH_2 electrodes.^[70]

Electrochemical performance of liquid battery and all-solid-state battery using MgH_2 anode are shown in Fig. 1-9 and Fig. 1-10, respectively.

The first issue is the significant volume change during long cycles, which leads to capacity fade. One approach is the use of nanostructured MgH_2 , which can help alleviate the effects of volume expansion by providing more surface area for lithium insertion and allowing for better mechanical flexibility, more uniform stress distribution can be achieved.^[71] Another approach involves the use of MgH_2 composites, where MgH_2 is combined with conductive materials such as carbon nanotubes, graphene, or other carbon-based materials to enhance electrical conductivity and supply space to accommodate volume expansion, thus improving cycling stability.^[14]

The second issue is the low electronic and ionic conductivity of MgH_2 . When using MgH_2 as active material, solid electrolytes and conductive additives are essential to be incorporated into the anode composite to provide ion conduction pathways and electron conduction pathways. However, this method significantly reduces the content of the active material, thereby lowering the overall energy density of the battery. This thesis also focused on the two challenges of MgH_2 and made a certain contribution.

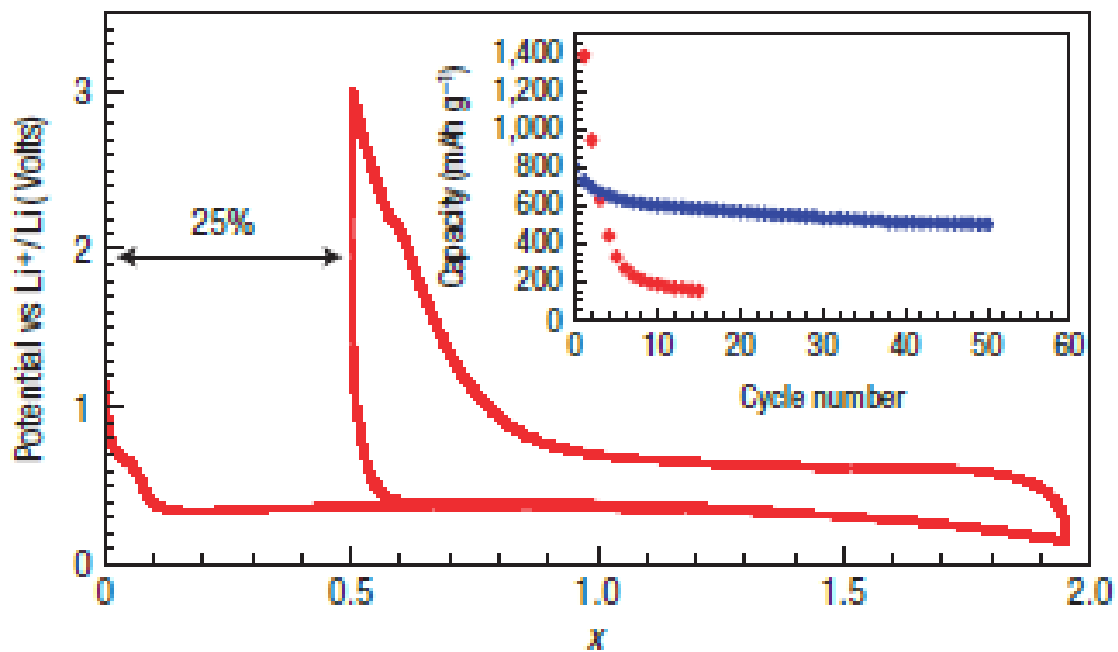


Figure 1-9. Electrochemical characterization of a MgH_2 electrode in liquid system. Inset: The corresponding reversible capacity versus the cycle number for the same cell cycled between 0.15 and 2.5 V in red and in blue. [64]

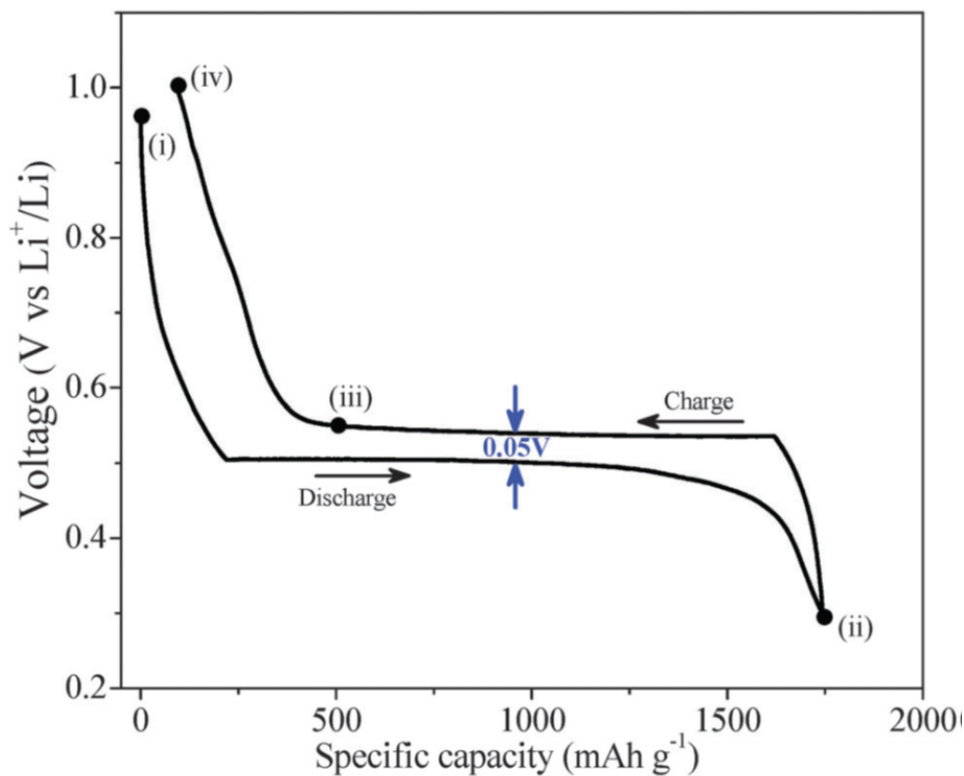
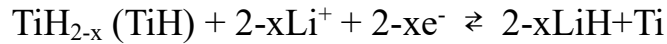
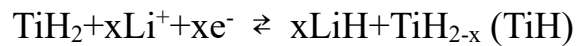


Figure 1-10. Electrochemical characterization of a MgH_2 electrode in all-solid-system battery. [26]

1.4.2 TiH₂ anode

Titanium hydride (TiH₂) is another widely researched metal hydride electrode. Compared to MgH₂, TiH₂ has a lower theoretical capacity (1074 mAh/g), but it features a lower reaction potential (0.15 V vs Li/Li⁺). As an anode material, it enables the battery to deliver a higher operating voltage, improving its power output. Moreover, Li and Ti do not form an alloy, meaning that even if the charging cutoff voltage is reduced to 0.05 V, the reversibility is still high.^[72] Although TiH₂ is also a conversion-type active material, its reaction mechanism differs slightly from that of traditional conversion-type anodes. Upon reacting with lithium, TiH₂ does not directly form Ti and LiH. Instead, it initially reacts with part of the lithium ions to produce TiH_{2-x} (TiH), followed by a further reaction between TiH_{2-x} and Li-ions to form Ti and LiH. The electrode reaction is exhibited below (charge-discharge curve is shown in Fig. 1-11):^[73]



Unlike MgH₂ which is an electronic insulator, TiH₂ possesses high electronic conductivity (Fig. 1-12), which could enable faster reaction kinetics. Its high electronic conductivity may also reduce the need for conductive additives in the electrode, as it can provide its own electron transport pathways. Additionally, the high density of TiH₂ suggests that batteries utilizing it could

achieve a higher volumetric energy density.^[74]

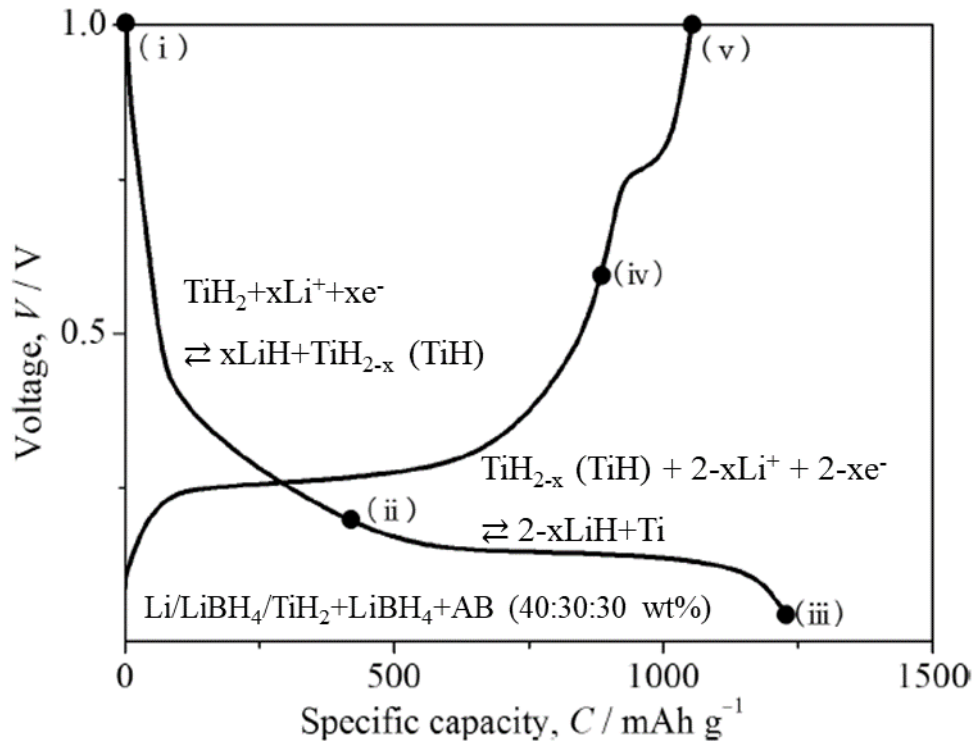


Figure 1-11. Electrochemical characterization of a TiH_2 electrode in all-solid-system battery. [72]

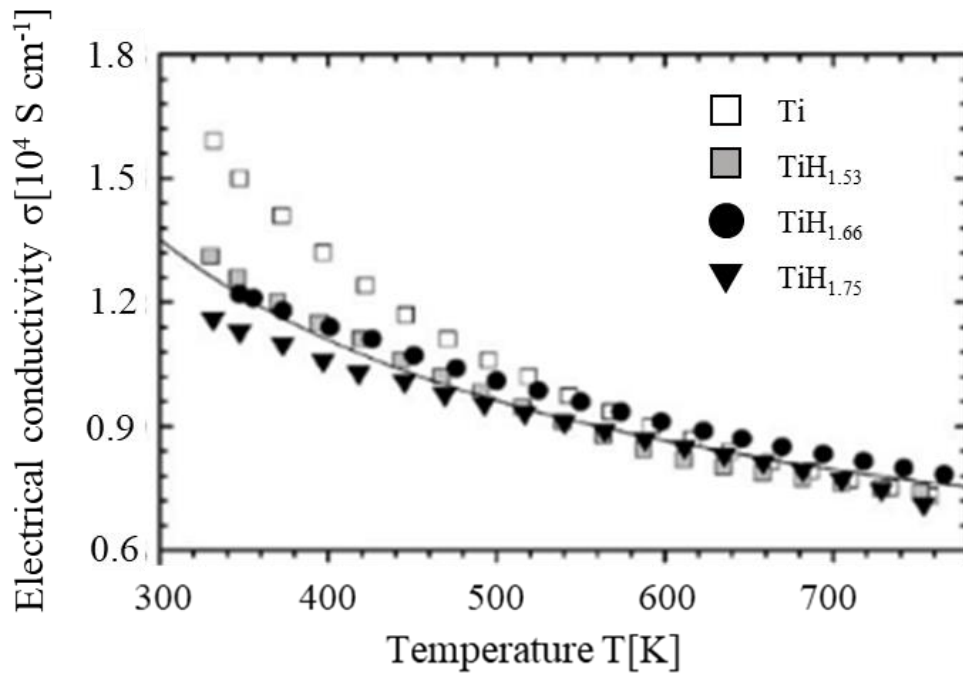


Figure 1-12. Electrical conductivity of Ti, $\text{TiH}_{1.53}$, $\text{TiH}_{1.66}$ and $\text{TiH}_{1.77}$. [74]

1.5 Solid Electrolytes *in situ* formed active materials

As described in 1.3.1, unlike liquid-based batteries, all-solid-state batteries require a certain proportion of solid electrolytes and conductive additives to be included in the electrode composite to provide ionic and electronic conductivity. However, since the battery capacity is determined by the content of active materials in the positive and negative electrodes, the key to achieving high capacity lies in how much the solid electrolyte and conductive additives in the electrodes can be reduced. To reduce the amount of electrolyte in the electrodes and achieve higher capacity in all-solid-state batteries, this thesis focused on the concept of "solid electrolytes *in situ* formed active material".

In this concept, when Li^+ ions are inserted into the electrode during the conversion reaction, a solid electrolyte in the form of a lithium salt (which is Li-ion conductor) is generated at the interface between the electrolyte and the electrode. This *in situ* formed solid electrolyte enables Li^+ to diffuse into the interior of the electrode, ensuring the utilization of the electrode. The schematic illustration of the solid electrolyte *in-situ* formation process was shown in Fig.1-13.

To demonstrate this solid electrolyte *in situ* formed electrode, Sato et al.

reported $\text{Mg}(\text{BH}_4)_2$, which generates the solid electrolyte LiBH_4 . Despite not containing a solid electrolyte in the initial electrode composite, $\text{Mg}(\text{BH}_4)_2$ exhibits an extremely low charge-discharge polarization of approximately 0.1 V and achieves charge-discharge capacities comparable to electrodes containing solid electrolytes.

This result suggests that ionic conduction pathways are formed in the electrode composite during the initial discharge of $\text{Mg}(\text{BH}_4)_2$. Measurements of the ^{11}B MAS-NMR spectra of $\text{Mg}(\text{BH}_4)_2$ electrode composites revealed a shift in the main peak position, indicating that $\text{Mg}(\text{BH}_4)_2$ generates LiBH_4 during the discharge process. The reaction formula of $\text{Mg}(\text{BH}_4)_2$ is exhibited below:



This discovery provides strong evidence for the feasibility of solid electrolyte *in situ* formed active material.^[75]

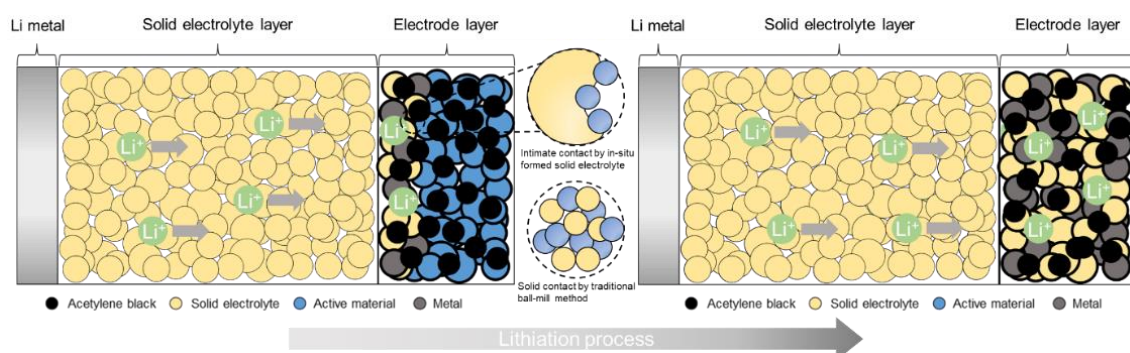


Figure 1-13. Schematic illustration of the solid electrolyte *in-situ* formation process in the electrode composite.

1.6 Research Objectives

With the growing societal demand for safer and higher energy density energy storage devices, all-solid-state batteries (ASSBs) have emerged as the primary choice for next-generation batteries due to their high safety and energy density. However, the commercialization of metallic lithium, considered the ultimate anode, faces significant challenges due to its high chemical reactivity and dendrite formation issues. This underscores the importance of exploring alternative anode materials.

An ideal anode material should possess characteristics such as high capacity, low potential, and long cycle life. As mentioned earlier, conversion-type electrodes generally exhibit high theoretical capacities. Among them, hydride-based anodes stand out due to the presence of lightweight hydrogen ions, which provide the highest theoretical capacity for the same metallic ion and relatively low potential. These attributes contribute significantly to enhancing the energy density of batteries. Although the significant volume changes associated with hydride anodes may lead to capacity fading during cycling, such capacity degradation is effectively mitigated in Chapter 5 of this thesis.

Importantly, by leveraging the electrolyte self-generation mechanism of conversion-type electrodes in combination with high-capacity hydride anodes, it is possible to create novel anodes with energy densities far

exceeding those of conventional graphite anodes in lithium-ion batteries. The primary objective of this thesis is to construct new hydride-based anodes for ASSBs, utilizing the *in situ* formed mechanism of solid electrolytes to achieve substantial energy density improvements. The main content of each chapter is outlined below.

Chapter 1 outlines the research background and introduces LIBs, ASSBs, metal hydride anodes and solid electrolyte *in situ* formed mechanism.

Chapter 2 discusses the charge-discharge performance and reaction mechanisms of novel solid electrolyte *in situ* formed active materials, including $\text{Ca}(\text{BH}_4)_2$ and MgH_2 . Among them, $\text{Ca}(\text{BH}_4)_2$, which has a lower potential compared to $\text{Mg}(\text{BH}_4)_2$, was able to undergo charge-discharge cycling even after the electrolyte was excluded from the electrode. However, it exhibited significant side reactions. In contrast, MgH_2 electrodes without any electrolyte also demonstrated excellent electrochemical performance, despite the *in situ* formed LiH having a conductivity of only 10^{-7} S/cm.

Chapter 3 focuses on enhancing battery energy density by increasing electrode thickness. Based on the $\text{Ca}(\text{BH}_4)_2$ and MgH_2 anodes discussed in Chapter 1, different active materials exhibited varying electrochemical characteristics with thicker electrodes. The $\text{Ca}(\text{BH}_4)_2$ electrode, benefiting from the high ionic conductivity of the self-generated LiBH_4 , showed no capacity degradation even with an electrode thickness of up to 435 μm ,

resulting in a significant increase in areal capacity. In contrast, the MgH_2 electrode displayed a notable decline in capacity with increased electrode thickness. Through electrochemical and XPS analyses, the reaction distribution within the thickened electrode was clarified.

Chapter 4 achieved a significant enhancement in energy density by substantially increasing the active material content within the electrode. The feasibility of TiH_2 as a novel solid electrolyte *in situ* formed active material was first validated and successfully demonstrated. Due to TiH_2 's high electronic conductivity and high capacity, it was used as a bifunction material, serving as both a conductive additive and an active material. By mixing TiH_2 with MgH_2 , electrodes with an active material content up to 90% were developed. Compared to existing hydride anodes, these electrodes exhibited a remarkable improvement in energy density.

Chapter 5 describes a new method to improve the cycling performance of hydride anodes by increasing electrode density. By mixing MgH_2 and Ti within the electrode and utilizing their spontaneous chemical reaction, the overall density of the electrode was significantly enhanced. The changes in the electrode's mechanical properties effectively suppressed the influences of volume changes from the active material. No noticeable cracks or voids observed in the electrode even after cycling. Even with a high active material loading of 90%, the electrode maintained over 95% of its initial capacity

after 200 cycles.

Chapter 6 give the main conclusions of the research.

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Chapter 2

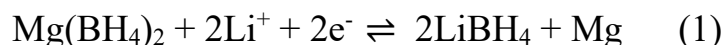
***In situ* Electrolyte Design: High-Capacity $\text{Ca}(\text{BH}_4)_2$ and MgH_2 Anodes for All-Solid-State Batteries**

2.1 Introduction

All-solid-state batteries (ASSBs) using non-flammable inorganic electrolytes instead of organic liquid electrolytes have attracted much attention as energy storage devices with high levels of safety and reliability.^[1] ASSBs facilitate the bipolar configurations which provide Li-ion batteries (LIBs) with a route to higher volumetric energy density (achieved by stacking multiple electric cells in series within a single package).^[2] The electrode compositions of commercial LIBs typically comprise more than 90% active material.^[3,4] Active materials with high electronic conductivity render carbon additives unnecessary in a composite electrode.^[5,6] However, in order to engender Li-ion and electron conductivity in an electrode in which the active material has both mediocre electronic and ionic transport properties, most reported electrode mixtures of ASSBs contain not only

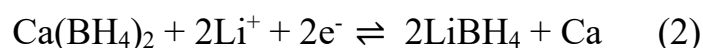
carbon additive but also solid electrolyte.^[7,8] This approach will decrease the energy density of an ASSB because the added solid electrolyte and carbon components do not directly contribute to the capacity of the battery. Therefore, if the content of active material in a composite electrode mixture can be maximized without losing ionic conductivity and compromising contact with the electrolyte, then, the energy density of an ASSB could be dramatically improved. This would represent an encouraging new strategy to composite electrode design.

Several studies adopting this kind of strategy have been performed in cells with a variety of chemistries.^[9–12] Among them, an ASSB design using an electrode layer without any conductive additives was reported by Nagao *et al* by blending Li₂SO₄ with transition metal oxides such as Li₂RuO₃^[9] or LiCoO₂^[11] as the active and electronically conducting material. Li₂SO₄ acts here so as to impart ionic conductivity to the active electrode material. Moreover, Sato *et al* reported an ASSB using Mg(BH₄)₂ and Acetylene black (AB) as a composite electrode without the necessity of the solid electrolyte as a component. The following conversion reaction occurred between Li⁺ and Mg(BH₄)₂:^[12]



Importantly a solid electrolyte is not required as part of a Mg(BH₄)₂ composite due to the *in situ* formation of electrolyte in the borohydride

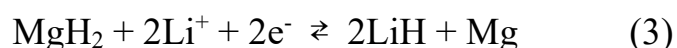
electrode during lithiation. This thus negates the need to add LiBH₄ electrolyte to the anode in advance (as might be performed otherwise). Therefore, the active material content can be significantly increased from 40% to 70% and an improved actual capacity can be achieved.^[12] Mg(BH₄)₂ operates at 0.8 V (vs. Li/Li⁺), which is not a suitable redox potential for the negative electrode of a high voltage battery. An active material with a lower electrochemical potential is strongly desirable to perform the role of generating the electrolyte *in situ*. In this work, HT-LiBH₄ is also the target for the *in situ* electrolyte because of its favorable ductility and high ionic conductivity (of 10⁻³ S cm⁻¹ above the orthorhombic (LT) -hexagonal (HT) phase transition at 115 °C).^[13,14] I therefore decided to focus on alternative borohydride-based salts (such as Ca(BH₄)₂, KBH₄, NaBH₄, etc.) as candidates for a suitable negative electrode material (that would generate LiBH₄ solid electrolyte *in situ*). Among them, Ca(BH₄)₂ is conspicuous in having a high theoretical capacity of 768 mAh g⁻¹. Moreover, Ca(BH₄)₂ has a lower electrochemical potential than that of Mg(BH₄)₂ given the presence of the Ca/Ca²⁺ redox couple. The assumed reaction of Ca(BH₄)₂ would follow:



theoretical capacity: 768 mAh g⁻¹

Considering the development of solid electrolyte *in situ* formed active

materials with a higher theoretical capacity, I focused on MgH₂ active material. MgH₂ boasts a remarkably high theoretical capacity of 2036 mAh/g and a reaction potential of approximately 0.5 V vs. Li/Li⁺, making it a suitable redox potential for use as an anode in lithium-ion batteries. From the perspective of improving energy density, it can be considered a highly advantageous active material. MgH₂ has already been reported as an anode material for lithium-ion batteries, and the following electrode reaction has been identified:



In this study, both Ca(BH₄)₂-AB and MgH₂-AB composites were prepared as negative electrodes by ball-milling. This investigation represents the first report of Ca(BH₄)₂ as an active anode component in an ASSB. Our experiments reveal an impressive electrochemical performance and demonstrate the feasibility of Ca(BH₄)₂ and MgH₂ towards *in situ* electrolyte formation.

2.2 Experimental

2.2.1. Materials Synthesis

The powdered starting materials, LiBH_4 (95%, Sigma-Aldrich), $\text{Ca}(\text{BH}_4)_2$ (95%, Sigma-Aldrich), AB (97%, Denka) and Boron (99%, Wako) were purchased and used without further purification. Two types of composite electrode materials (with or without LiBH_4 electrolyte; hereafter named samples **1** and **2** respectively) were prepared by ball-milling. For the latter composite electrode without electrolyte included (sample **2**), a mixture of $\text{Ca}(\text{BH}_4)_2$ and AB in a weight ratio of 70:30 was placed into a zirconia milling jar (45 ml) with zirconia balls (diameter: 3 mm) weighing 18 g (to give a ball:powder weight ratio of 36:1). The electrode mixture was milled at a rotation speed of 600 rpm for 2 h using a FRITSCH Pulvarisette 7 planetary mill. The composite electrode mixture including electrolyte (sample **1**) was prepared from $\text{Ca}(\text{BH}_4)_2$, LiBH_4 and AB with a weight ratio of 40:30:30. using otherwise the same milling conditions employed for sample **2**. MgH_2 (95 %, Fuji Film Wako) electrodes were prepared by same condition with a different rotation speed of 400 rpm for 30 min. The composite electrode materials with or without LiBH_4 electrolyte are named samples **3** and **4**, respectively.

2.2.2. Half cell assembly

Coin cells fitted with a polyether ether ketone (PEEK) sleeve were used in all electrochemical measurements. All-solid-state half cells were fabricated using a Li metallic disc counter electrode, a LiBH₄ solid electrolyte layer and either composite electrode **1**, **2**, **3** or **4** with a weight of 6 mg. An Li metallic disc (Honjo Metal Co., LTD; diameter: 8 mm) was formed using a belt punch and was pressed by hand above a stainless steel (SS) plate (diameter: 10 mm). SS was used as the current collector. A layer of LiBH₄ electrolyte was added and uniaxially pressed at 255 MPa. The respective composite electrodes were placed on top of the LiBH₄ electrolyte and pressed at 318 MPa to complete the three-layered cell before sealing.

2.2.3. Electrochemical measurements

Each ASSB was charged and discharged galvanostatically at 120 °C using a Hokuto Denko-HJ1020mSD8 battery tester. Each cell was thus heated above the orthorhombic-hexagonal phase transition temperature of LiBH₄ (using an electric furnace inside Ar globe box). All charge-discharge measurements of sample **1** and **2** were performed using a current density and voltage range of 0.5 mA cm⁻² and 0.2-1.4 V (vs. Li/Li⁺), respectively. All charge-discharge measurements of sample **3** and **4** were performed using a current density and voltage range of 0.5 mA cm⁻² and 0.3-1.0 V (vs. Li/Li⁺),

respectively.

2.2.4. Characterization

Measurements by *ex-situ* powder X-ray diffraction (XRD) (Rigaku RINT-TTRIII), magic angle spinning nuclear magnetic resonance spectroscopy (MAS NMR) (JNM-ECA400), *ex-situ* X-ray absorption spectroscopy (XAS) (SAGA-LS BL12, total fluorescence yield mode) and *ex-situ* X-ray photoelectron spectroscopy (XPS) (JEOL JPS-9010MC/IV equipped with monochromatic Mg K α radiation at 1253.6 eV) were performed at room temperature in order to identify the charge and discharge products and hence to assess the reaction mechanism of the Ca(BH₄)₂-based electrodes (The split in the binding energy between Ca 2p_{1/2} and 2p_{3/2} is 3.5 eV. The FWHM of the fitted doublets of different states are 2.26 eV (Initial and lithiated state) and 1.95 eV (delithiated state). The height ration between 2p_{1/2} and 2p_{3/2} is 0.51:1 (2p_{1/2} : 2p_{3/2}). The C1s peak (284.6 eV) was used for calibration.). Since both LiBH₄, Ca(BH₄)₂ and MgH₂ are air- and moisture-sensitive, all operations (cell construction, charge-discharge measurement and other analyses were conducted under Ar atmosphere (dew point; lower than -80 °C, oxygen; lower than 1 ppm))

2.3 Results and Discussion

2.3.1. Electrochemical Performance

The all-solid-state half cells based on electrodes containing LiBH_4 electrolyte (sample 1) show a large reversible capacity of 327 mAh g^{-1} and exhibit a plateau at approximately 0.3 V vs. Li/Li^+ in the charge curve (i.e. during lithiation as $\text{Ca}(\text{BH}_4)_2$ is charged with Li) (Fig. 2-1(a)). To the best of our knowledge, this is the first report of the use of $\text{Ca}(\text{BH}_4)_2$ as an anode material for an LIB. Compared to other reported BH_4^- based active materials, a larger difference in the charge and discharge voltage was observed; i.e. 0.6 V for $\text{Ca}(\text{BH}_4)_2$ as compared with 0.1 V for $\text{Mg}(\text{BH}_4)_2$,^[12] which indicates a higher resistance for the former in the respective charge-discharge process. Moreover, it is notable that the initial charge (lithiation) capacity of 424 mAh g^{-1} is significantly lower than the theoretical capacity of 768 mAh g^{-1} (as would be expected from equation 2). This indicates that other factors such as possible side reactions or impurities could inhibit the electrode reaction (a topic that I return to below). Importantly, and as anticipated, when compared to the redox potential of $\text{Mg}(\text{BH}_4)_2$ (*ca.* 0.8 V vs. Li/Li^+), $\text{Ca}(\text{BH}_4)_2$ exhibited a lower average voltage of close to 0.6 V vs. Li/Li^+ . In principle, this wider potential range could be attractive for a prospective anode material for a high

voltage battery.

By comparison, Fig. 2-1(b) shows the charge-discharge profile of the composite electrode fabricated without added LiBH_4 electrolyte (sample **2**). This specimen exhibits an initial charge capacity of 470 mAh g^{-1} and an initial reversible capacity of 417 mAh g^{-1} . Clearly, the electrode performance does not suffer notably from the omission of the electrolyte with no decrease in capacity observed. Hence appreciable ionic conductivity is imbued to the sample **2** by the electrolyte formed *in situ* during the lithiation process. Moreover, the actual capacity (i.e. capacity of the entire electrodes), which is shown in the upper x-axes of Fig. 2-1 (a, b), for sample **2** (331 mAh g^{-1}) is much larger than the actual capacity of sample **1** (170 mAh g^{-1}) because of the increased content of active material in the electrode layer of the former.

A steep slope is apparent in the initial charging curve from 1.2 V to 0.5 V. A similar slope has also been observed in other ASSBs in which LiBH_4 has been used as the solid electrolyte. The distinctive feature is tentatively assigned to the formation of an SEI between the active materials and LiBH_4 in the electrode layer.^[15,16] The content of LiBH_4 in sample **2** is less than that of sample **1**, therefore the capacity assigned to this slope for sample **2** is 53 mAh g^{-1} which is smaller than the value of 77 mA h g^{-1} for sample **1**. To investigate the origin of the plateau present at *ca.* 0.75 V in the 2nd lithiation curve, charge-discharge measurements were performed for sample **1** using

voltage ranges of 0.2 V~1.4 V and 0.2 V ~1.0 V (Fig. 2-2). A small plateau is clearly observable at 0.75 V in the 2nd lithiation curve. After changing the discharge cut-off voltage to 1.0 V in the 3rd delithiation curve, the plateau at 0.75 V disappeared in the 4th lithiation curve, indicating this plateau is associated with the reversible capacity of the slope above 1.0 V in the delithiation process. However, the higher capacity attributable to the slope above 1.0 V suggests this higher voltage feature has some relation to the plateau at 0.8 V. The cycling performance of sample **1** is shown in Fig. 2-1(c). Most significantly, when compared to the performance of sample **2** shown in Fig. 2-1(d), the cycling capability of sample **1** did not improve when electrolyte was added to the electrode mixture. After 25 cycles, the capacity decayed to *ca.* 190 mAh g⁻¹ which is considerably lower than that of sample **2** over an equivalent period (*ca.* 260 mAh g⁻¹). This result indicates that the interface between the active materials and the solid electrolyte in sample **2** is more intimate and stable as a result of the *in situ* formation of LiBH₄ than that achieved by ball-milling the respective borohydrides at the outset in sample **1**. The coulombic efficiency during cycling is also shown in Fig. 2-1(c,d). Both electrodes reach high efficiency quickly and there is no significant difference between sample **1** and sample **2** over 25 cycles. It was considered that the relatively large volume expansion of Ca(BH₄)₂ (143%) may be the main reason of capacity degradation along with cycling.

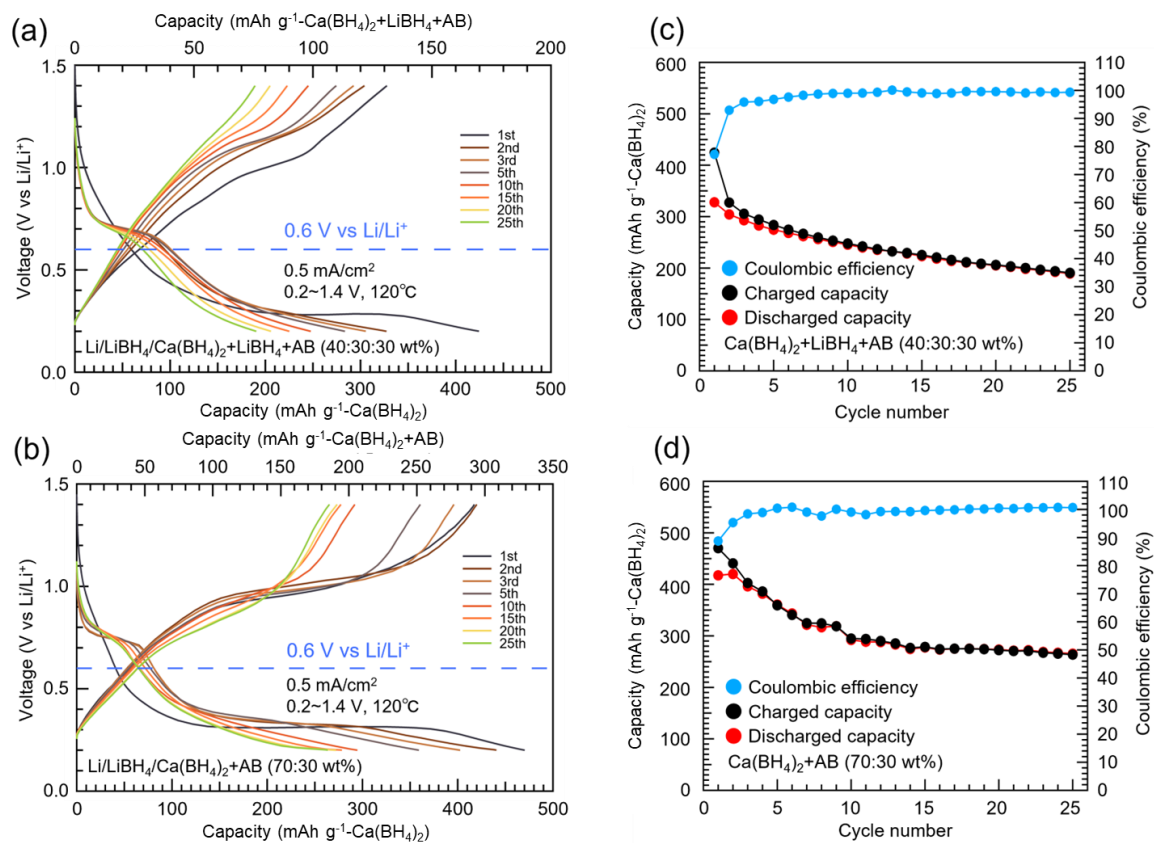


Figure 2-1. (a) Charge-discharge voltage profiles for sample 1 (initially 40:30:30 wt.% $\text{Ca}(\text{BH}_4)_2:\text{LiBH}_4:\text{AB}$); (b) charge-discharge voltage profiles of sample 2 (initially 70:30 wt.% $\text{Ca}(\text{BH}_4)_2:\text{AB}$); (c, d) cycling performance of sample 1 and sample 2, respectively. The charge-discharge experiments were measured with a current density of 0.5 mA cm^{-2} at 120°C.

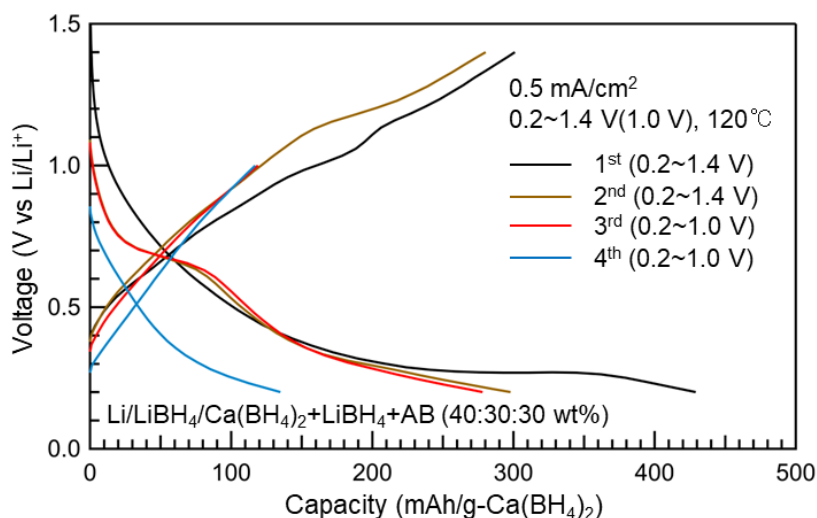


Figure 2-2. Charge-discharge voltage profiles of sample 1 (initially 40:30:30 wt.% $\text{Ca}(\text{BH}_4)_2$: LiBH_4 : AB) with voltage ranges of 0.2~1.4 V and 0.2~1.0 V vs Li for cycles 1-2 and 3-4, respectively.

In contrast, charge-discharge performance of MgH_2 anodes were shown in Fig. 2-3. From Fig. 2-3(a), the initial discharge capacity of sample **3** was determined to be 1738 mAh/g, and the reversible capacity was 1685 mAh/g. These values align with previously reported results for MgH_2 all-solid-state batteries. Notably, in the charge curve, it was observed that the plateau near 0.8 V became longer with increasing cycles. This phenomenon has been observed not only in MgH_2 systems but also in other hydride active materials such as TiH_2 . Additionally, when a liquid-based battery was assembled using an MgH_2 anode, it was reported that the 0.8 V plateau disappeared. This suggests that the 0.8 V plateau arises from some reaction between MgH_2 and the LiBH_4 solid electrolyte or the presence of a region with a different

overpotential.

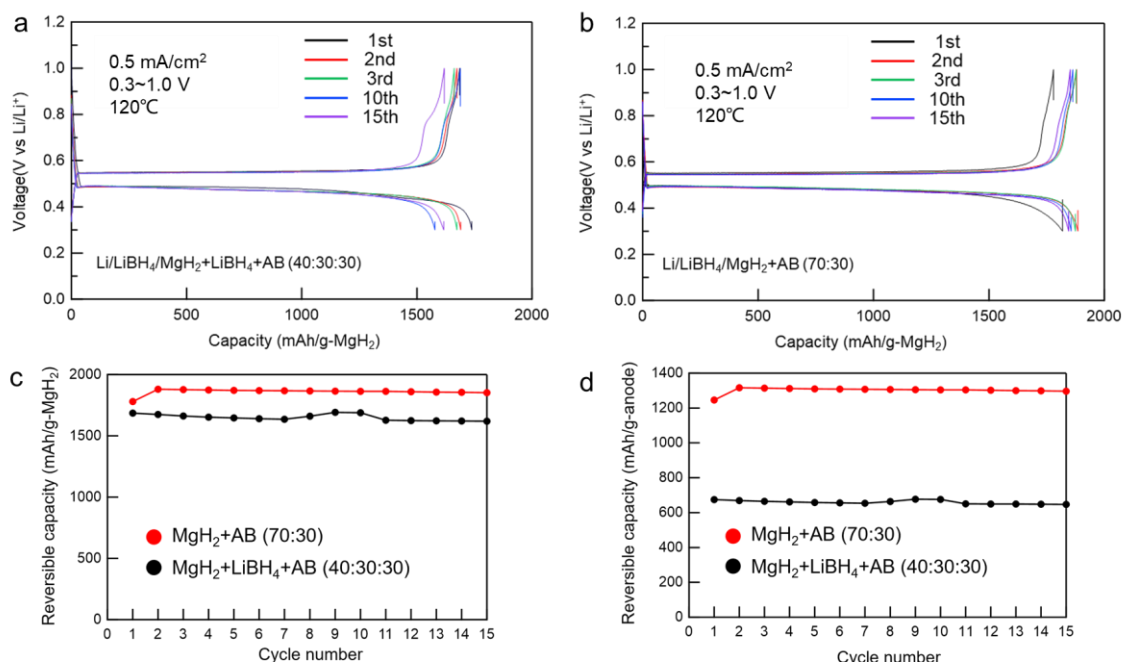


Figure 2-3. (a) Charge-discharge voltage profiles for sample 3 (initially 40:30:30 wt.% MgH_2 : LiBH_4 :AB); (b) charge-discharge voltage profiles of sample 4 (initially 70:30 wt.% MgH_2 :AB); (c, d) cycling performance of reversible capacity based on mass of MgH_2 and anode, respectively. The charge-discharge experiments were measured with a current density of 0.5 mA cm^{-2} at 120°C .

Fig. 2-3(b) shows the charge-discharge curves and cycle performance of an electrode composite that does not contain LiBH_4 (sample 4). The initial discharge capacity was 1818 mAh/g, and the reversible capacity was 1780 mAh/g, both of which are higher than the sample containing LiBH_4 . This higher capacity is likely due to the more uniform distribution of the electrochemically *in situ* formed electrolyte compared to the mechanical mixture of active material and solid electrolyte. In the charge curve of the electrolyte-free electrode, a plateau near 0.8 V was also observed, but it was significantly shorter than that of the electrode containing LiBH_4 . This shorter

plateau is presumed to be caused only by the interface between the electrolyte layer and the electrode layer. Similar to sample **3**, a flat plateau at 0.5 V and a very low charge-discharge voltage hysteresis of approximately 0.1 V were observed. Despite the absence of a solid electrolyte in the initial state of the electrode, these low values suggest that MgH_2 generates a solid electrolyte during the discharge process, enabling Li^+ to diffuse throughout the electrode via the generated solid electrolyte. Additionally, Fig. 2-3(c,d) shows the capacities per active material and the actual capacities up to the 15th cycle for $\text{MgH}_2+\text{LiBH}_4+\text{AB}$ (40:30:30 wt%) and MgH_2+AB (70:30 wt%). It was found that the electrolyte-free electrode exhibited significantly higher actual capacity.

2.3.1. Reaction Mechanism

In order to investigate whether LiBH_4 is formed inside the electrode layer in the lithiation process, *ex-situ* XAS measurements were performed. The XANES (X-ray Absorption Near Edge Structure) spectra for sample **2** at various states of (dis)charge are illustrated in Fig. 2-4. Spectra of pure $\text{Ca}(\text{BH}_4)_2$ and LiBH_4 are also shown for comparison. In the initial (pre-lithiated) state, the peak at 190.9 eV in the B K-edge XANES spectrum (Fig. 2-4(a)) approximately matches with the maximum (190.9 eV) and edge positions in the equivalent spectrum for $\text{Ca}(\text{BH}_4)_2$ and very closely resembles

previously reported spectra.^[17] After lithiation (charging), the absorption edge energy shifts to 191.4 eV which is almost identical to the position of the edge in the equivalent XANES spectrum for LiBH₄.^[18] This strongly indicates the formation of LiBH₄, which would result from the reaction between Li and Ca(BH₄)₂ as proposed in equation 2. After delithiation (discharging), the peak following the absorption edge is broadened with a maximum that shifts towards a lower photon energy. However, the position (and shape) of this peak in the spectrum of the sample in the delithiated state is not entirely consistent with the spectrum of Ca(BH₄)₂ (which once more is expected to show a maximum at 190.9 eV). This result from the delithiated state measurement indicates that the system is not completely reversible and that the materials do not entirely return to Ca(BH₄)₂. It was assumed that this result might be attributed to an irreversible side reaction that occurs during the charge-discharge process. From an examination of the Li K-edge XANES spectra (Fig. 2-4(b)), the lithiated sample shows a well-defined peak at 59.3 eV which is entirely consistent with the Li K-edge spectrum for the reference sample of bulk LiBH₄. This peak does not appear in the Li K-edge spectrum for the sample in the de-lithiated state. These observations are therefore consistent with the formation of LiBH₄ during the lithiation process and its subsequent consumption during delithiation. The combined XAS results indicate that the *in situ* formation of ionically-conducting electrolyte

is possible within the electrode containing the $\text{Ca}(\text{BH}_4)_2$ active material. It should also be noted that since both LiBH_4 and $\text{Ca}(\text{BH}_4)_2$ are moisture-sensitive, the peaks that appear at *ca.* 194 eV in the B K-edge spectra and at approximately 64 eV in the Li K-edge spectra can be considered to be the result of the reaction of the borohydrides with air. By reference to previous studies, I can attribute the peaks that appear at *ca.* 194 eV in the B K-edge spectra to B_2O_3 or LiBO_2 , and the peaks at approximately 64 eV in the Li K-edge spectra likely originate from LiBO_2 or Li_2O .^[18,19]

It is necessary to gain further understanding of the electrochemical reaction of $\text{Ca}(\text{BH}_4)_2$, which has not been clarified, *ex-situ* XRD measurements were performed at three different points of the charge-discharge cycling process; (i) the initial state (prior to cycling), (ii) the

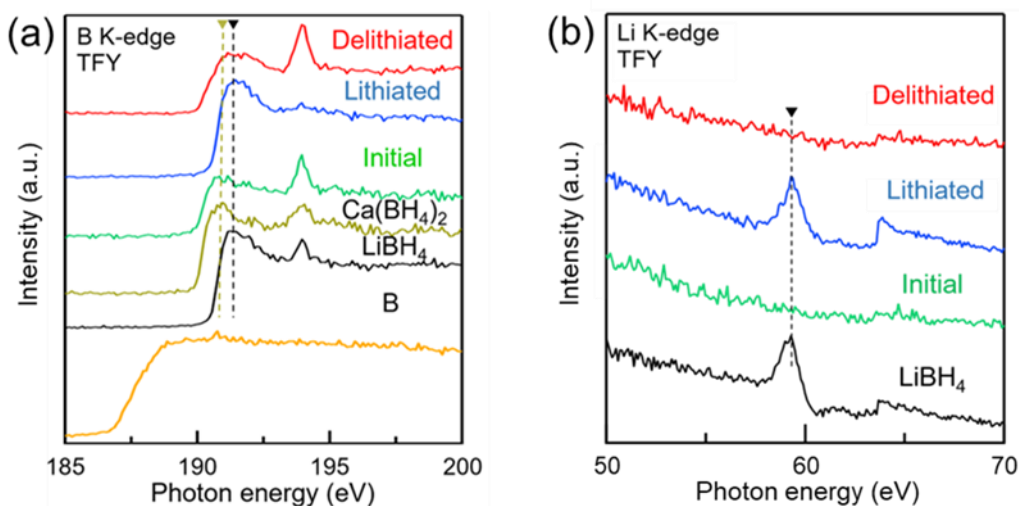


Figure 2-4. Ex-situ total fluorescence yield (TFY) mode XAS measurements of a $\text{Ca}(\text{BH}_4)_2$ -AB composite electrode (2) in various charge states. (a) B K-edge spectra (black dashed line: LiBH_4 , yellow dashed line: $\text{Ca}(\text{BH}_4)_2$) and (b) Li K-edge spectra (black dashed line: LiBH_4).

lithiated state (after the first charge) and (iii) the de-lithiated state (after the first discharge) (Fig. 2-5). All of the samples used a double layer cell (LiBH₄ electrolyte layer/Ca(BH₄)₂ electrode layer) for XRD measurement. The initial sample (prior to cycling) contains Ca(BH₄)₂ as anticipated. The relatively broad peaks observed for the Ca(BH₄)₂ phase are expected from the ball milling process (causing both particle size reduction and likely microcrystalline strain).^[20] For comparison, the experimental XRD pattern of the Ca(BH₄)₂ starting material can be found in Fig. 2-6. The diffractogram of this starting material shows that two phases of Ca(BH₄)₂ are initially present; the α -Ca(BH₄)₂ (orthorhombic) and β -Ca(BH₄)₂ (tetragonal) polymorphs. After ball milling, β -Ca(BH₄)₂ remains and α -Ca(BH₄)₂ is replaced by γ -Ca(BH₄)₂ (orthorhombic). Once Li reacts with Ca(BH₄)₂ to form the lithated electrode, there is no longer any evidence for Ca(BH₄)₂ peaks in the diffraction pattern suggesting that all of the calcium borohydride is consumed. However, no Ca metal peaks are observed in the lithiated electrode sample as would be expected from equation 2 and, in fact, peaks characteristic of CaH₂ appear and are especially noticeable in the 2 θ range

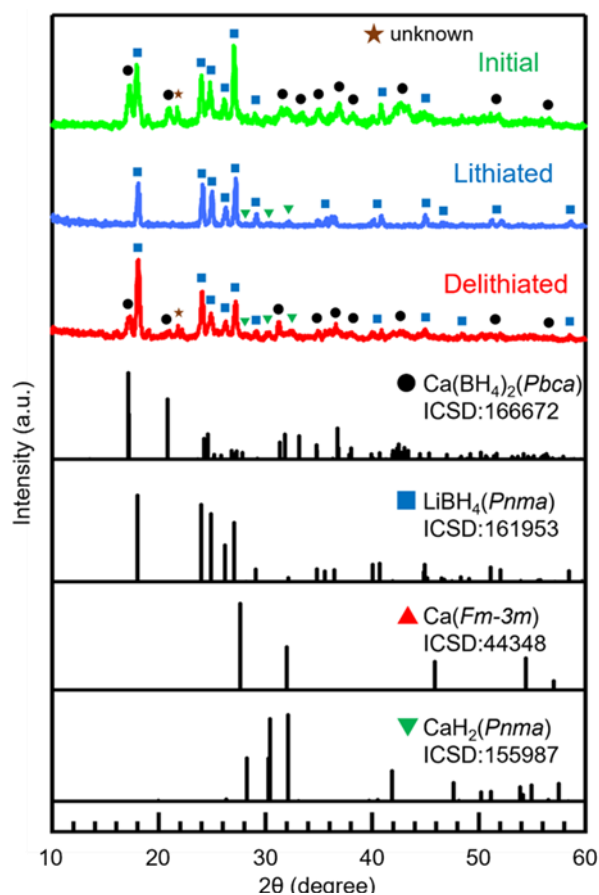
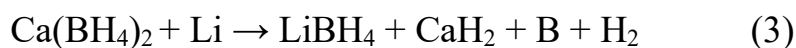


Figure 2-5. Comparison of ex-situ XRD patterns before and after the initial charge-discharge cycles of a $\text{Ca}(\text{BH}_4)_2\text{:AB}$ (70:30 wt.%) composite electrode (2). Patterns generated from structures of possible products within the ICSD are shown for reference.

of $28^\circ\text{--}32^\circ$. This result would suggest that either the electrode reaction is not that anticipated in equation 2 or that a side reaction occurs after lithiation is complete (and before the next delithiation cycle).

If the experimental electrode reaction does not follow the proposed process identified in equation 2, the reaction between Li and $\text{Ca}(\text{BH}_4)_2$ can result in the direct formation of CaH_2 .

For example:





All of these hypothetical reactions are accompanied with the formation of boron. Hence, the presence of free boron in the lithiated state would indicate the occurrence of one or more of these reactions during the de-lithiation process.

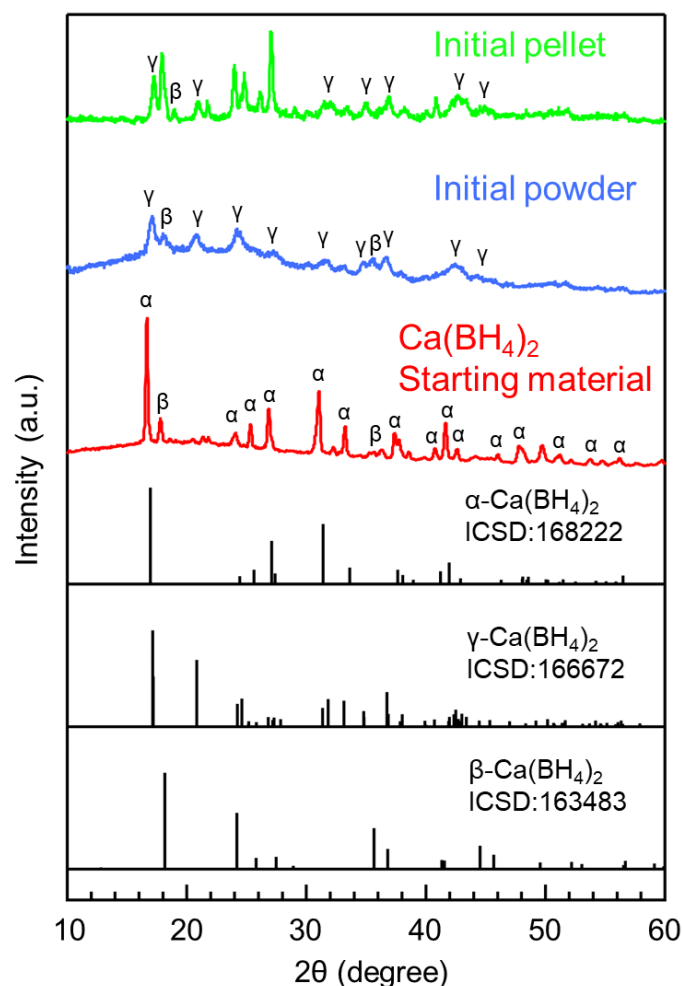


Figure 2-6. *Ex-situ* XRD patterns of: (a) the commercial $\text{Ca}(\text{BH}_4)_2$ starting material; (b) the commercial borohydride powder following ball milling and (c) a pellet (formed from the milled powder). Patterns generated from ICSD entries for $\text{Ca}(\text{BH}_4)_2$ phases are shown below and marked as α : $\alpha\text{-Ca}(\text{BH}_4)_2$ (orthorhombic), β : $\beta\text{-Ca}(\text{BH}_4)_2$ (tetragonal), γ : $\gamma\text{-Ca}(\text{BH}_4)_2$ (orthorhombic).

Solid state MAS NMR measurements were performed on sample **2** and compared to spectra measured for commercial $\text{Ca}(\text{BH}_4)_2$ and boron itself to establish whether boron is formed during the electrode reaction (Fig. 2-7). The ^{11}B MAS NMR spectra taken across a range from 700 to -700 ppm are shown in Fig. 2-7(a). The sharp peaks in the initial and lithiated states do not bear any resemblance to those from elemental boron. Considering Fig. 2-7(b), which focuses on the resonances within a range of 10 to -50 ppm, commercial $\text{Ca}(\text{BH}_4)_2$ presents two peaks at chemical shifts of -30 and -33 ppm. These peaks originate from two different polymorphs of $\text{Ca}(\text{BH}_4)_2$. Minella *et al* reported that the signal at -30 ppm corresponds to the orthorhombic structure of the α -polymorph, whereas that at -33 ppm can be assigned to the tetragonal β -polymorph of the borohydride.^[21] These findings are consistent with our XRD measurements which reveal that the as-received borohydride is a mixture of both α - $\text{Ca}(\text{BH}_4)_2$ and β - $\text{Ca}(\text{BH}_4)_2$. In the lithiated state, Li reacts with $\text{Ca}(\text{BH}_4)_2$ and the ^{11}B MAS NMR spectrum reveals a strong peak at -41 ppm which is almost identical to the reported spectrum for LiBH_4 .^[12] Strikingly, however, a sharp line at -0.1 ppm, which would be characteristic of boron, is not observed in the spectrum of the lithiated sample. These results suggest that B is not formed during the lithiation process. $\text{Ca}(\text{BH}_4)_2$ peaks emerge again in the delithiated state. The peak in this spectrum that can be observed at -41 ppm corresponds again to

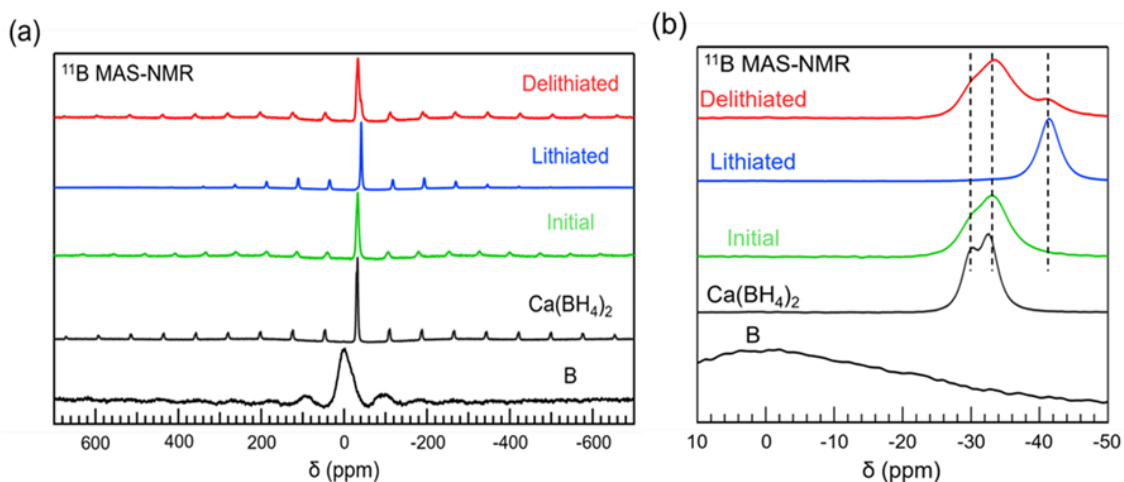


Figure 2-7. Solid state ^{11}B MAS NMR spectra taken from sample 2 in different charge states as compared to pure boron and $\text{Ca}(\text{BH}_4)_2$ showing: (a) spectra over the full spectral window and (b) expanded spectra from 10 to -50 ppm.

LiBH_4 and its appearance is somewhat inevitable given that LiBH_4 from the electrolyte layer will be present when the sample is prepared for NMR measurements.

In order to probe the possibility of boron formation still further, *ex-situ* EXAFS (Fig. 2-4(a)) at the B L-edge region was also performed. A peak which would be consistent with free elemental boron is not observed in any of the samples in the initial, lithiated or de-lithiated states, indicating free boron does not form during charge-discharge. This observation is thus consistent with the result of MAS NMR measurement. From the combined experimental evidence, it seems unlikely, therefore, that reactions which lead to B and CaH_2 (such as equations 3-5) occur on lithiation

To examine the possible reasons behind the presence of CaH_2 in the cell, the lithiated electrode (sample 2) was left to stand for 3 h at 120 °C in the Ar

glove box prior to XRD measurement (Fig. 2-8). Evidently, the intensities of the CaH_2 peaks increase significantly after this time period (as compared with an electrode normally at rest for only ca. 1 minute at 120 °C after lithiation and before *ex-situ* characterisation). Therefore, I tentatively propose that CaH_2 continues to form from the reaction between Ca and LiBH_4 during the period of time following lithiation, given also that the cell is at a temperature of 120 °C. Rationally, there are other examples of CaH_2 formation when using $\text{Ca}(\text{BH}_4)_2$, for example, when $\text{LiBH}_4/\text{CaBH}_4$ composites were heat treated and when $\text{Ca}(\text{BH}_4)_2/\text{THF}$ electrolyte was used with Ca metal electrodes, demonstrating the high reactivity of Ca metal.^[22,23] Given that no diffraction peaks or ^{11}B resonances from any solid state boron-containing compounds are detected, it might be speculated that diborane (B_2H_6) gas, which is a typical thermal decomposition product of borohydrides, is formed and released, thus accounting for the apparent boron deficit.^[23,24] The formation of B_2H_6 will be clarified by evolved gas analysis using mass spectroscopy in future studies. No new peak corresponding to compounds contained Li was observed in the Fig. 2-8 (XRD patterns of lithiated state rest for 3h after lithiation process), indicating the amorphous structure of byproduct contained Li atom. However, it is difficult to identify the chemical formula.

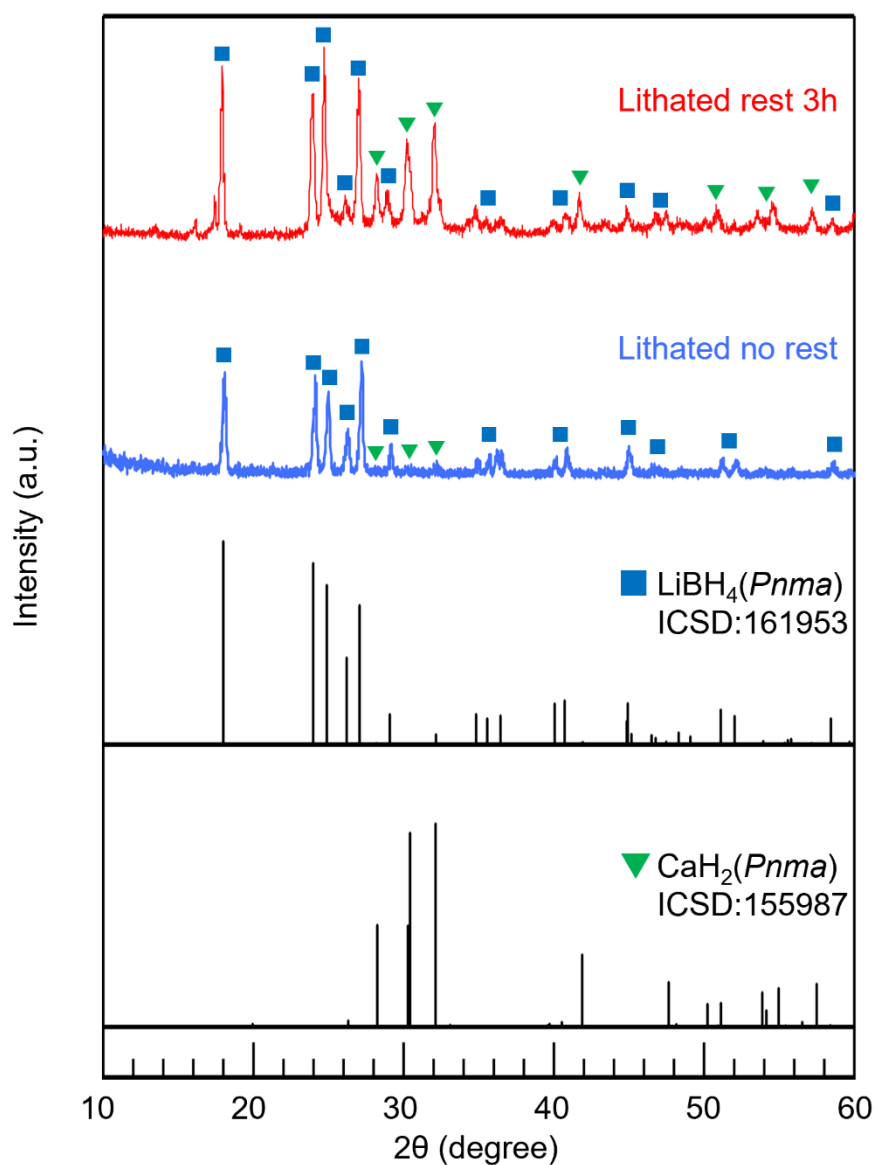


Figure 2-8. Comparison of *ex-situ* XRD patterns of sample 2 in the lithiated state with and without a “rest period” (3 h rest at open circuit voltage - OCV) between cycles. The CaH_2 peaks grow in relative intensity after the 3 h “rest period”.

Ca metal is not observed in the XRD patterns of samples taken in the lithiated state. This suggests that if Ca metal is formed during the lithiation process then the metal likely possesses a nanocrystalline or amorphous

structure. When discharging the cell, $\text{Ca}(\text{BH}_4)_2$ peaks emerge again in the XRD patterns from delithiated samples, which is also consistent with the result of ^{11}B MAS NMR measurements. It is worthwhile mentioning, however, that the CaH_2 peaks remain even after delithiation, indicating that the reaction between Ca and LiBH_4 , in the lithiated state, is irreversible and so it is not possible for the lithiated products to then reform $\text{Ca}(\text{BH}_4)_2$ completely. As is clear from the diffraction patterns in Fig. 2-5, peaks originating from LiBH_4 were observed in all samples irrespective of (dis)charge state, but as noted above, from the nature of the XRD samples taken from the cells, it is not possible to distinguish whether the LiBH_4 is present in the electrode layer (having formed from $\text{Ca}(\text{BH}_4)_2$ during lithiation) or it originates from the electrolyte layer itself.

Given the apparent absence of Ca in lithiated materials by XRD, further clarification was sought to test the premise that Ca is a reaction product of Li and $\text{Ca}(\text{BH}_4)_2$ as postulated in equation (2). *Ex-situ* XPS measurements of the initial, lithiated and delithiated states of sample **2** were performed. The Ca 2p XPS spectra are displayed in Fig. 2-9 (The split in the binding energy between $2p_{1/2}$ and $2p_{3/2}$ is 3.5 eV. The FWHM of the fitted doublets of different states are 2.26 eV (Initial and lithiated state) and 1.95 eV (delithiated state). The height ration between $2p_{1/2}$ and $2p_{3/2}$ is 0.51:1 ($2p_{1/2} : 2p_{3/2}$)). In the initial state (corresponding to $\text{Ca}(\text{BH}_4)_2$), two characteristic

peaks are observed at 351 eV and 347.5 eV, which correspond to the $2p_{1/2}$ and $2p_{3/2}$ spin-orbit doublets. After lithiation, the Ca 2p peaks are shifted to lower binding energy, appearing at 349.8 eV and 346.3 eV respectively. These latter peak positions are consistent with the XPS spectrum from metallic Ca(0),^[25] indicating that formation of Ca metal does indeed occur during the lithiation process. In the delithiated state, the characteristic peaks Ca 2p peaks return to the higher binding energies characteristic of Ca(II) in $\text{Ca}(\text{BH}_4)_2$. As indicated by the *ex-situ* XAS measurements, the lithiated products do not return entirely to $\text{Ca}(\text{BH}_4)_2$ due to the consumption of Ca to form CaH_2 (on reaction with LiBH_4).

The proposed reaction mechanisms at the $\text{Ca}(\text{BH}_4)_2$ electrode might be summarized as below:

1. *Lithiation process:*

Li^+ reacts with $\text{Ca}(\text{BH}_4)_2$ to form Ca metal and LiBH_4 . according to eq. (2).

2. *Period between charge and discharge:*

Active Ca metal reacts with LiBH_4 to form CaH_2 impurity irreversibly. (Boron-containing by-products are also formed; most likely gaseous B_2H_6)

3. *Delithiation process:*

Remaining Ca metal reacts with LiBH_4 to form $\text{Ca}(\text{BH}_4)_2$.

Given the irreversible CaH_2 formation between charge and discharge, a fraction of the lithiated product (LiBH_4) does not return reversibly to $\text{Ca}(\text{BH}_4)_2$ and capacity is lost in the reverse reaction:

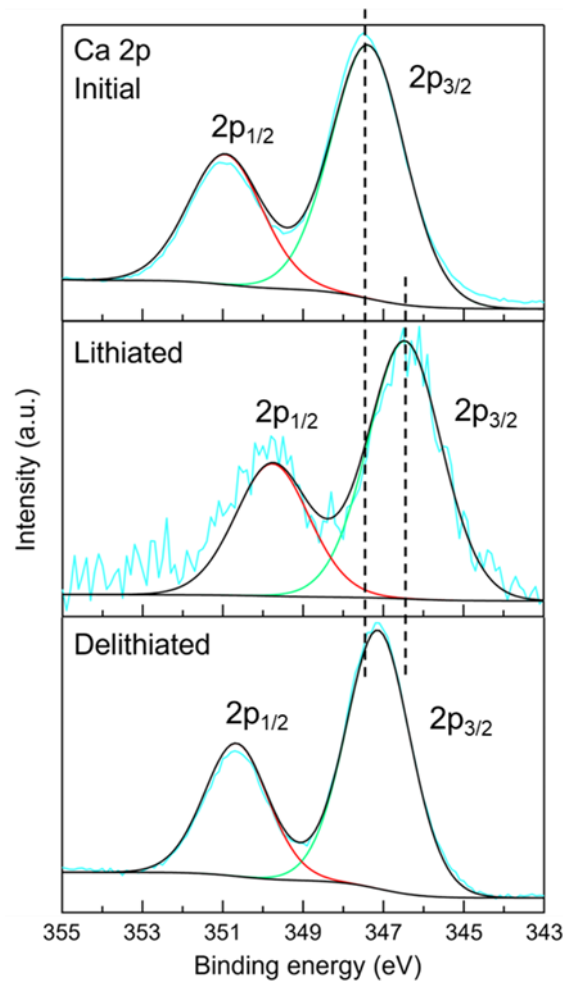
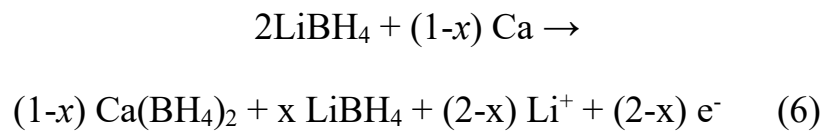


Figure 2-9. *Ex-situ* Ca 2p XPS measurement of a $\text{Ca}(\text{BH}_4)_2$ -AB composite electrode in various charge states.

It is interesting to note that in the equivalent $\text{Mg}(\text{BH}_4)_2/\text{Li}$ system no impurity such as MgH_2 was detected (by XRD or otherwise).^[12] Given the possibility of metal hydrides acting as negative electrodes, I sought to consider the influence of CaH_2 as a possible active material and its contribution to the total capacity. To investigate this hypothesis I constructed an all-solid-state cell using CaH_2 as the active material under charge/discharge conditions employing a current density of 0.05 mA cm^{-2} and an operating temperature of 120°C . From the charge-discharge curves of CaH_2 (Fig. 2-10), it can be seen that a reversible capacity of only 16 mAh g^{-1} was obtained. These observations reinforce the premise that CaH_2 does not contribute meaningfully to the capacity of the $\text{Ca}(\text{BH}_4)_2$ electrode.

However, in order to validate whether the performance could be affected

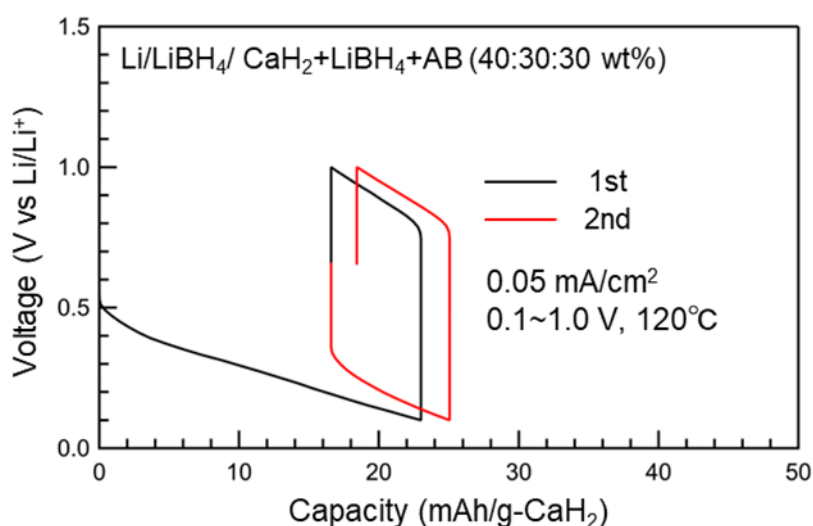


Figure 2-10. Charge-discharge voltage profiles of a CaH_2 - LiBH_4 -AB electrode composite (initially 40:30:30 wt.% CaH_2 : LiBH_4 :AB).

by an increased proportion of CaH_2 within the *composite* borohydride electrode (**2**), I performed a series of galvanostatic intermittent titration test (GITT) measurements. As shown in Fig. 2-11, I included a “rest period” of 6 h after every constant current charge process. With the exception of a slightly higher polarization, the performance of this battery was not dramatically influenced by the increased amount of CaH_2 contained in the electrode layer. These results suggest that the amount of CaH_2 formed in the cells with the electrode composition of **2** is not appreciable enough to impede the active material $\text{Ca}(\text{BH}_4)_2$ substantially. Further, the results indicate that polarization effects are not significant in these cells (despite the consideration that CaH_2 has poor electronic conductivity with a band gap of 5.84 eV).^[26] It is nevertheless worth noting that the Coulombic efficiency of this battery (ie. rested for 6 h) is only 85%, which is lower than the 90% efficiency achieved for sample **2** (which is at rest for only 1 min between discharging and charging). Hence there is a direct link between the rest time and Coulombic efficiency (reversibility) as a progressively greater proportion of lithiated products (i.e. Ca) are consumed during the rest period.

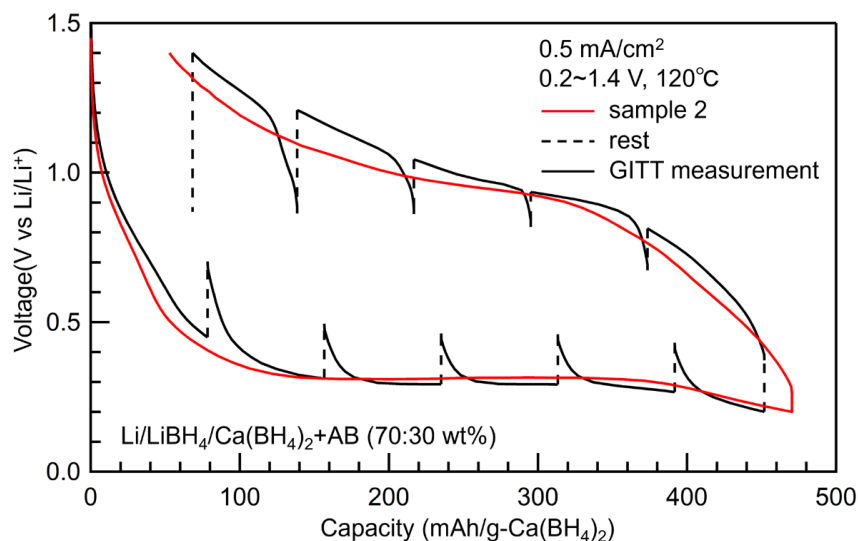


Figure 2-11. GITT profiles of a $\text{Ca}(\text{BH}_4)_2$ -AB composite electrode (2) following a 6 h “rest period” (black lines; constant current charge-discharge at 0.5 mA cm^{-2} for 50 min followed by application of an OCV for a “rest period” of 6 h). The discharge-charge curve for sample 2 without applying such a “rest period” is superimposed for comparison (red line).

2.4 Conclusions

$\text{Ca}(\text{BH}_4)_2$ has been utilized as a negative electrode material in a rechargeable LIB for the first time. The borohydride electrodes show a large charge capacity of 470 mAh g^{-1} despite evident polarization effects. The results indicate that $\text{Ca}(\text{BH}_4)_2$ should be more suitable than $\text{Mg}(\text{BH}_4)_2$ for the fabrication of high voltage LIB given its lower redox potential of 0.6 V vs. Li/Li^+ . Moreover, importantly, because of the *in situ* formation of LiBH_4 during the lithiation process, no solid electrolyte component is required in the fabricated composite electrode (i.e. only the active material and activated

carbon are required) and the actual capacity can be significantly improved from 170 to 331 mAh g⁻¹. Meanwhile, MgH₂ was also verified as the solid electrolyte *in situ* formed active material to charge-discharge even the ionic conductivity of LiH is low. Compared to established approaches in which the electrolyte is combined with the active electrode material by ball-milling, it was considered that an electrolyte formed *in situ* provides superior interfacial contact between the active electrode materials and the solid electrolyte. Closer probing of the charge/discharge process reveals that CaH₂ impurity (itself only partially reversible and contributing close to negligible capacity to the battery) is formed during cycling and that this appears to occur principally at the time *between* charge and discharge; minimizing these “rest periods” therefore reduces the scale of impurity formation.

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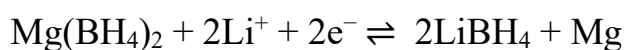
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Chapter 3

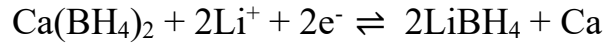
For Improving Energy Density of Electrolyte *in-situ* Formed Anodes- Investigation on Charge–Discharge Performance and Reaction Distribution of Thickened Electrode

3.1 Introduction

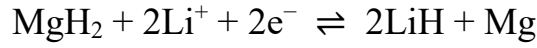
From Chapter 1 and previous study, $\text{Mg}(\text{BH}_4)_2$, $\text{Ca}(\text{BH}_4)_2$, MgH_2 , and MgCl_2 have been reported as solid electrolytes that form an active anode material *in situ*.^[1–3] All of the anode composites consisted only of active material and acetylene black (AB), with no additional electrolytes, because the ionic conductors LiBH_4 , LiH , and LiCl were formed *in situ*.^[1–3] The conversion reactions between Li and active materials are described as



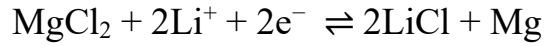
(theoretical capacity: 993 mAh g^{-1}) (1)



(theoretical capacity: 768 mAh g⁻¹) (2)



(theoretical capacity: 2036 mAh g⁻¹) (3)



(theoretical capacity: 562 mAh g⁻¹) (4)

Among them, LiBH₄ exhibits a high ionic conductivity of 10⁻³ S cm⁻¹ at temperatures greater than 115°C because of its orthorhombic-to-hexagonal phase transition ^[4,5] and LiH and LiCl exhibit electrical conductivities of 10⁻⁷ and 5.9×10⁻⁵ S cm⁻¹ even at 120°C.^[3,6] Compared with active material–LiBH₄–AB composite electrodes, MgH₂–AB, Mg(BH₄)₂–AB, Ca(BH₄)₂–AB, and MgCl₂–AB composite electrodes have the advantage of exhibiting almost no capacity degradation (electrode composite load: 7.64 mg cm⁻²) even without the addition of electrolytes.

Increasing the thickness of electrodes is expected to improve the energy density of batteries because the relative volume of the current collector and solid electrolyte layer will be minimized.^[7–9] To further improve the energy density of batteries, incorporating a thicker electrode that includes an active material that forms a solid electrolyte *in situ* is an attractive strategy. Under this approach, not only the relative volume of the electrode layer but also the loading amount of active materials in batteries should be increased. However,

the resistance of the electrode also increases with increasing electrode thickness, limiting the ion or electron transport in thick electrodes.^[10] MgCl₂–AB composite electrodes with a thickness of 180 μm exhibited a 1st charge capacity of 297 mAh g⁻¹, which is lower than the corresponding 465 mAh g⁻¹ capacity of a 50 μm -thick electrode, indicating that long-distance migration of Li⁺ ions is difficult.^[3] Hence, to increase the energy density, further investigations of the electrochemical performance and reaction mechanism of thick electrodes with different active materials that form a solid electrolyte *in situ* are necessary. The present work focuses on MgH₂ as an active material because of its high theoretical capacity of 2036 mAh g⁻¹.^[11] For comparison, the charge–discharge performance of Ca(BH₄)₂ and Mg(BH₄)₂, which form LiBH₄ (10⁻³ S cm⁻¹ at 120°C) *in situ*, is also characterized.^[1]

MgH₂–AB electrodes with various thicknesses ranging from 91 to 420 μm were prepared, and their charge–discharge behavior was investigated. Unfavorable degradation of the charge–discharge performance was observed in batteries with thick electrode layers. This result is inconsistent with the results for Mg(BH₄)₂, and I attribute this inconsistency to the difference in Li⁺-ion conductivity between LiBH₄ and LiH. Our experiments systematically reveal the reaction mechanism and distribution of a MgH₂–AB thick electrode for the first time. The electrochemical performance and

characterization results for thick MgH_2 -AB, $\text{Mg}(\text{BH}_4)_2$ -AB, and $\text{Ca}(\text{BH}_4)_2$ -AB electrodes are discussed in the Results and Discussion section.

3.2 Experimental

3.2.1. Electrode Preparation

The electrode composites without LiBH_4 electrolyte were prepared by ball-milling commercially acquired MgH_2 (95%, Fuji Film Wako) and AB (97%, Denka) under an Ar atmosphere. A powder (0.5 g) of MgH_2 and AB mixed in a mass ratio of 70:30 was loaded into a zirconia milling jar (45 mL) together with 18 g of zirconia balls (diameter: 3 mm). The electrode mixture was milled at a fixed rotation speed of 400 rpm for 30 min using a FRITSCH Pulvarisette 6 planetary mill. An electrode composite with LiBH_4 electrolyte was prepared using commercial MgH_2 , LiBH_4 (95%, Fuji Film Wako), and AB combined in a mass ratio of 40:30:30. For comparison, $\text{Mg}(\text{BH}_4)_2$ (95%, Sigma-Aldrich)-AB electrode composites and half-cells (used Li_2S - P_2S_5 as the solid electrolyte) were fabricated under the aforementioned conditions using electrodes with different thicknesses. Li_2S - P_2S_5 was prepared by ball-milling acquired Li_2S (99.9%, Sigma-Aldrich) and P_2S_5 (99%, Sigma-Aldrich) in a molar ration of 80:20. The mixture was ball-milled at a fixed rotation of 370 rpm for 20h with 18 g of zirconia balls and 0.5 g of mixtures.

For the $\text{Ca}(\text{BH}_4)_2$ -AB electrode, a mixture of $\text{Ca}(\text{BH}_4)_2$ and AB in a weight ratio of 70:30 was placed into a zirconia milling jar (45 ml) with zirconia balls (diameter: 3 mm) weighing 18 g (to give a ball:powder weight ratio of 36:1). The electrode mixture was milled at a rotation speed of 600 rpm for 2 h.

3.2.2. Half cells assembly

The all-solid-state MgH_2 and $\text{Ca}(\text{BH}_4)_2$ half-cells were assembled with a metallic Li (Honjo Metal) disc counter electrode, a LiBH_4 solid electrolyte layer, and MgH_2 and $\text{Ca}(\text{BH}_4)_2$ composite electrodes with and without the LiBH_4 electrolyte incorporated. For $\text{Mg}(\text{BH}_4)_2$ half-cells, Li-In alloy and Li_2S - P_2S_5 were used as counter electrode and solid electrolyte layer. Each all-solid-state cell (diameter: 10 mm) was assembled under Ar using an insulating cell die (polyether ether ketone, PEEK) sandwiched between two stainless steel rods. To vary the thickness of the electrode layer, different masses (4.5–30 mg) of the electrode components were used in half-cells with the same previously described configuration. On the basis of the pressed 20 mg electrode powders (20 mg: 280 μm (MgH_2), 20 mg: 290 μm ($\text{Ca}(\text{BH}_4)_2$)), the electrode thicknesses corresponding to different electrode weights were calculated; all of the electrodes were pressed at 318 MPa. The Li/ LiBH_4 / MgH_2 ($\text{Ca}(\text{BH}_4)_2$) half-cells were fabricated using the following

sequence. First, a Li metallic disc (Honjo Metal; diameter: 8 mm) was formed using a belt punch and was pressed by hand onto a stainless steel (SS) plate (diameter: 10 mm) used as a current collector. Powdered LiBH_4 electrolyte was added, and the resultant assembly was pressed at 318 MPa. To complete the three-layered cell, the respective MgH_2 or $\text{Ca}(\text{BH}_4)_2$ composite electrodes were placed on top of the LiBH_4 electrolyte and the whole assembly was pressed at 318 MPa.

3.2.3. Electrochemical Measurement

The electrochemical performance of each ASSB was evaluated at 120°C (above the orthorhombic-to-hexagonal phase transition temperature of LiBH_4) using a Hokuto Denko HJ1020mSD8 battery tester. All cycling experiments were conducted at a current density of 0.5 mA cm^{-2} within the potential range from 0.3 to 1.0 V and 0.2 to 1.4 V(vs. Li/Li^+) for MgH_2 and $\text{Ca}(\text{BH}_4)_2$. The electronic conductivity was measured by DC (direct-current) polarization method at 120°C using an electrochemical workstation (Biologic, VSP).

3.2.4. Characterization

Ex situ XRD measurements were carried out with a Rigaku RINT-TTRIII diffractometer emitting $\text{Cu K}\alpha$ radiation; samples were scanned over the 2θ

range 10° – 60° . Ex situ XPS (X-Ray Photoelectron Spectroscopy) measurements were performed at room temperature using a JEOL JPS-9010MC/IV spectrometer equipped with a monochromatic Mg K α radiation source (1253.6 eV). Cross-sectional XPS measurements were carried out with a Shimadzu KRATOS ULTRA2 spectrometer equipped with an Al K α radiation source (1486.6 eV). A 110 μ m X-ray beam (aperture) was used to measure the chemical state of electrode cross-sections. After each measurement, X-ray beam was moved 30 μ m toward the solid electrolyte side in preparation for the next measurement. The C 1s peak at 284.6 eV was used for calibration of all the acquired XPS data. All operations (cell assembly, charge–discharge experiments, and other analyses) were conducted under an Ar atmosphere.

3.2 Results and Discussion

3.3.1. Electrochemical Performance

For the purpose of maximizing the energy density of an ASSB, there are clear advantages in using as thick an electrode layer as possible. Therefore it is useful to investigate whether the electrolyte formed *in situ* would extend to the entire electrode layer if the thickness is increased (and conversely, therefore, whether the concept breaks down at a maximum thickness level).

The charge-discharge curves and cycle performance of a half-cell using a 290 μm -thick $\text{Ca}(\text{BH}_4)_2$ electrode layer (produced by an electrode mixture of 20 mg) are shown in Fig. 3-1(a). This cell exhibited an initial reversible capacity of 373 mAh g^{-1} and a charge capacity of 425 mAh g^{-1} that did not decay dramatically when compared to sample **2** in chapter 1 (which utilized 6 mg of electrode mixture giving a thickness of 87 μm and an initial reversible capacity of 417 mAh g^{-1}). Encouragingly, when the amount of electrode mixture is increased still further to 30 mg, giving a calculated electrode thickness of 435 μm , the cell still shows a high initial charge capacity of 418 mAh h g^{-1} and continues to act reversibly (Fig. 3-1(b)). In practical terms, the 30 mg electrode is much thicker than the vast majority of those reported in ASSBs,^[12–14] and the results imply that the electrode reaction successfully proceeds via the *in situ* formation of electrolyte even with an electrode layer approaching $\frac{1}{2}$ mm.

To investigate the battery performance of the MgH_2 –AB electrodes with

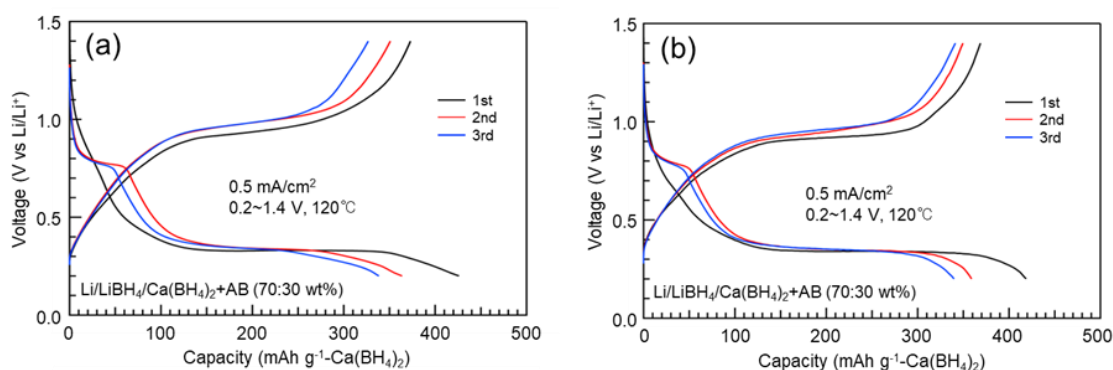


Figure 3-1. Charge-discharge voltage profiles of a $\text{Ca}(\text{BH}_4)_2$ -AB composite electrode in which the electrode thickness was increased to: (a) 290 μm (electrode mixture of 20 mg) and (b) 435 μm (electrode mixture of 30 mg).

different thicknesses, I conducted galvanostatic charge–discharge measurements (Fig. 3-2). The charge–discharge profile of a half-cell with a 63 μm -thick $\text{MgH}_2\text{--AB}$ electrode (Fig. 3-2(a)) shows that the first charge and reversible capacity are 1570 and 1493 mAh g^{-1} , respectively, and that the coulombic efficiency is 94.7%. The initial discharging process shows a clear plateau (constant-voltage region) at 0.5 V, corresponding to the hydride conversion reaction of MgH_2 (equation 2). In the discharge curve, a small plateau at 0.8 V vs. Li/Li^+ is observed and tentatively attributed to a side reaction between MgH_2 and LiBH_4 .^[15] For comparison, Fig. 3-2(b) shows the charge–discharge profiles of the half-cell with a 6 mg $\text{MgH}_2\text{--AB}$ electrode composite (electrode thickness: 84 μm). The initial lithiated capacity of 1628 mAh g^{-1} and reversible capacity of 1553 mAh g^{-1} are comparable to those of the 4.5 mg $\text{MgH}_2\text{--AB}$ electrode, indicating that the electrochemical performance of the batteries is not affected by an increase in the electrode thickness when the electrode layer is less than 100 μm thick.

To understand the influence of thicker ($>100\ \mu\text{m}$) electrode layers on the charge–discharge performance, the $\text{MgH}_2\text{--AB}$ electrode mixtures with 10 mg (140 μm), 20 mg (280 μm), and 30 mg (420 μm) were tested under the same conditions (Fig. 3-2(c-e)). First-charge capacities of 1237, 603, and 425 mAh g^{-1} were obtained. Due to the initial charging capacity, for $\text{MgH}_2\text{--AB}$ electrodes with masses of 4.5 mg, 6 mg, 10 mg, 20 mg and 30 mg, the value

of C-rate corresponding to 0.5 mA cm^{-2} is 0.06 C, 0.045 C, 0.027 C, 0.0135 C and 0.009 C, respectively. Importantly, the initial charge capacity of these batteries decreased significantly with increasing thickness of the electrode layer. All of the cells with a MgH_2 –AB electrode exhibit almost the same difference of $\sim 0.1 \text{ V}$ between the charge and discharge voltages. This similarity suggests that the resistances in the charge–discharging process might not substantially differ among batteries fabricated using electrodes with different thicknesses. In addition, the low overpotential of MgH_2 electrode should be affected by other factors other than Li-ion conductivity, such as H^- conductivity.^[16]

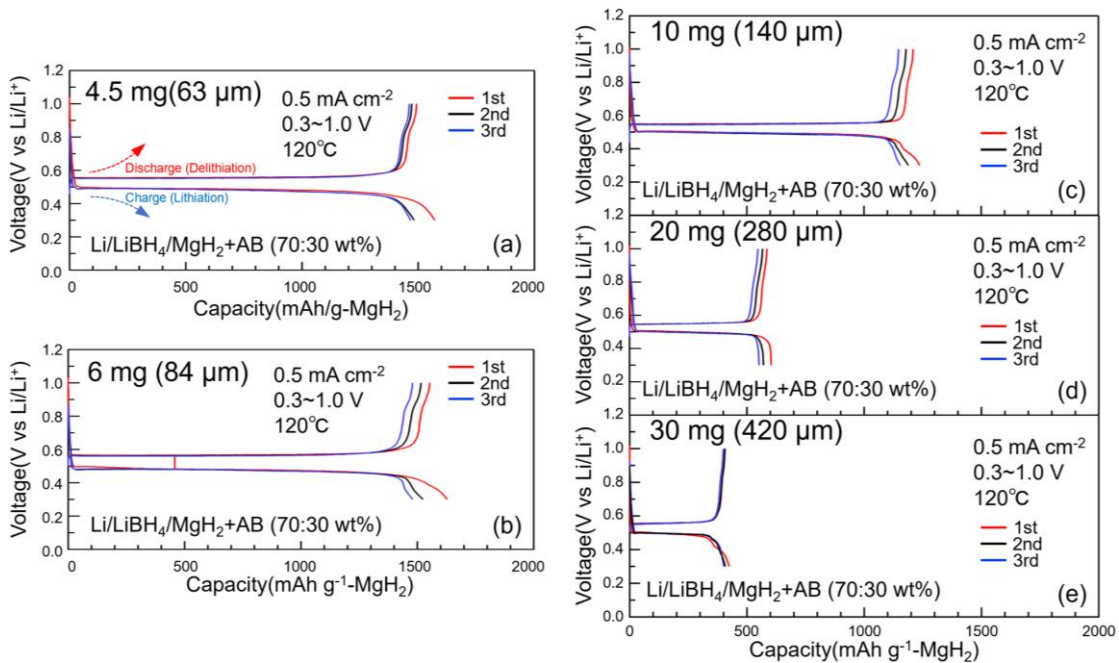


Figure 3-2. Charge–discharge voltage profiles of a MgH_2 electrode (initially 70:30 wt% MgH_2 :AB) with an anode mass loading of (a) 4.5, (b) 6, (c) 10, (d) 20, and (e) 30 mg.

Obviously, there is a big difference between $\text{Ca}(\text{BH}_4)_2$ -AB and MgH_2 -AB electrodes. And the such a capacity retention of $\text{Ca}(\text{BH}_4)_2$ electrode with increased electrode thickness is not universally observed in “*in situ*” LIB solid electrolyte systems. For example, MgCl_2 exhibits a significant decrease in the initial lithitated capacity when the thickness of the electrode layer is increased.^[17] Comparing these results demonstrates that the ionic conductivity of the *in situ* solid electrolyte plays an essential role in the charge-discharge performance of the composite electrode (LiH : $\sigma = 10^{-7} \text{ S cm}^{-1}$ at 120°C , LiCl : $\sigma = 5.9 \times 10^{-5} \text{ S cm}^{-1}$ at 120°C ^[17] and LiBH_4 : $\sigma \approx 10^{-3} \text{ S cm}^{-1}$ at 120°C).

3.3.2. Reaction Mechanism

For investigate, the extent of the electrochemical reaction across the thicker ($290 \mu\text{m}$) $\text{Ca}(\text{BH}_4)_2$ electrode layer was probed *via ex-situ* XAS measurements performed on lithiated samples (Fig. 3-3). The B K-edge XANES spectra (Fig. 3-3(a)) showed evidence of a peak at 191.4 eV , which is in close agreement with the equivalent spectrum of the original thinner lithiated electrode (using an electrode mixture of 6 mg) and once again matches well to the LiBH_4 reference material. Furthermore, comparison of the Li K-edge XANES spectra (as shown in Fig. 3-3(b)) shows that the peak at 59.3 eV in the lithiated thick electrode sample (electrode mixture of 20

mg) is in a virtually identical position to the Li K-edge XANES spectra of both the LiBH_4 bulk reference and the original lithiated thin electrode sample (produced from an electrode mixture of 6 mg). The XAS results thus strongly indicate that LiBH_4 is formed *in situ* across the entire electrode layer, even when increasing the thickness by more than 290 μm .

To investigate the factors that contributed to the decrease of battery capacity with increasing MgH_2 electrode layer thickness, I acquired *ex situ* XRD (X-ray diffraction) patterns at the initial, 1st lithiated, and 1st delithiated states of the 84 and 280 μm -thick MgH_2 –AB electrodes (Fig. 3-4). The

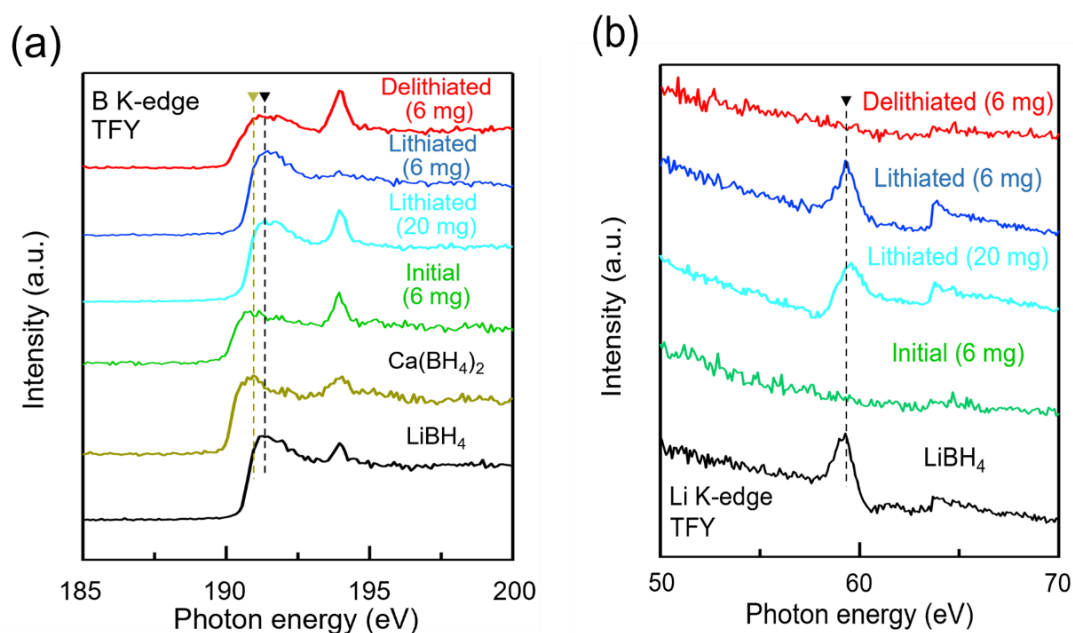


Figure 3-3. *Ex-situ* total fluorescence yield (TFY) mode XAS measurement of the $\text{Ca}(\text{BH}_4)_2$ -AB composite electrodes (fabricated from electrode mixtures of 6 mg and 20 mg, respectively) in various charge states, showing: (a) B K-edge spectra (black dashed line: LiBH_4 , green/yellow dashed line: $\text{Ca}(\text{BH}_4)_2$) and (b) Li K-edge spectra (black dashed line: LiBH_4).

double layer pellets of $\text{LiBH}_4/\text{MgH}_2$ electrode were used for the XRD measurement to maintain consistency, because the LiBH_4 cannot be completely separated from the charge-discharged cells. In the pattern corresponding to the initial state, except for the peaks of LiBH_4 in the electrolyte layer, only the peaks of the MgH_2 active material were observed. After the lithiation process of $\text{MgH}_2\text{-AB}$ electrode, in the pattern corresponding to the 280 μm -thick electrode in the lithiated state, five diffraction peaks appear at 32.19° , 34.4° , 36.62° , 47.83° , and 57.37° , which are assigned to metallic Mg. The initial lithiated capacity is only 603 mAh g^{-1} (theoretical capacity: 2036 mAh g^{-1}), suggesting that the active material did not react completely. These results explain why diffraction peaks of MgH_2 are also observed in the pattern corresponding to the 280 μm -thick electrode in the lithiated state. In the pattern of the 84 μm -thick electrode in the lithiated state, Metallic Mg peaks emerged at the same 2θ angles but with a higher intensity than those in the pattern of the 280 μm -thick electrode in the lithiated state, indicating that the ratio of Metallic Mg to MgH_2 in the lithiated state increased because of the high charge capacity (1628 mAh g^{-1}) of the cell with the 84 μm -thick electrode.

To further clarify the reaction mechanism, I carried out Rietveld refinements of the XRD data corresponding to the 84 and 280 μm -thick electrodes in the lithiated state (Fig. 3-5). From the content of MgH_2 and Mg

obtained by Rietveld analysis, the ratio of reacted MgH_2 /total MgH_2 is calculated as 83.7% and 24.8% for the 84 μm -thick electrode and 280 μm -thick electrode, respectively. These values are consistent with the values of 79.9% and 29.6% based on the charge capacity and theoretical capacity, respectively. Therefore, the substantial decrease in charge capacity is attributed to a large amount of unreacted MgH_2 that did not contribute to the battery capacity. The reasons behind the change in the intensity ratio of LiBH_4 will be studied in the future research.

After the delithiation process, MgH_2 peaks emerge again and the peaks corresponding to metallic Mg disappear. These results suggest that the MgH_2 –AB electrode is highly reversible even in cases of a thick electrode layer, consistent with the results of the charge–discharge measurements. Because the theoretical capacity of MgH_2 is substantially greater than that of other commercial active materials, I considered the possibility that the Li storage capacity of metallic Li is insufficient for the electrode reaction to proceed. The charge–discharge measurement of a double Li (11 mg)/ LiBH_4 /20 mg MgH_2 –AB electrode was also carried out (Fig. 3-6). The charge–discharge performance was not improved by the increase in the amount of metallic Li, revealing that the decrease in capacity of thick

electrodes is not caused by insufficient Li in the counter electrode.

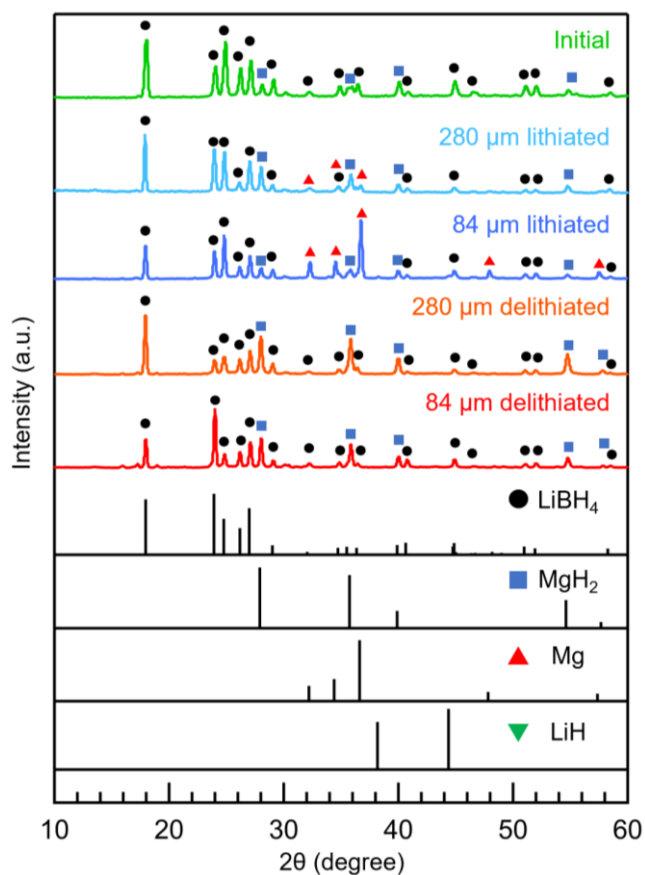


Figure 3-4. Comparison of *ex situ* XRD patterns before and after the initial charge–discharge cycles of 6 and 20 mg $\text{MgH}_2\text{:AB}$ (70:30 wt%) composite electrodes. The patterns generated from structures of possible products included in the ICSD are shown for reference. (LiBH_4 ICSD: 095207, MgH_2 ICSD: 155807, Mg ICSD: 77908, LiH ICSD: 61751)

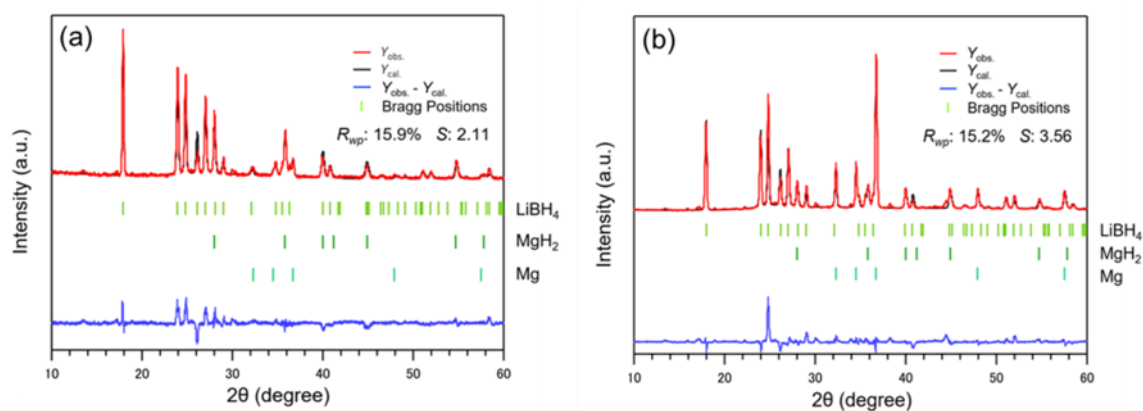


Figure 3-5. Rietveld refinement plots for (a) a lithiated 280 μm -thick $\text{MgH}_2\text{--AB}$ electrode and (b) an 84 μm -thick $\text{MgH}_2\text{--AB}$ electrode.

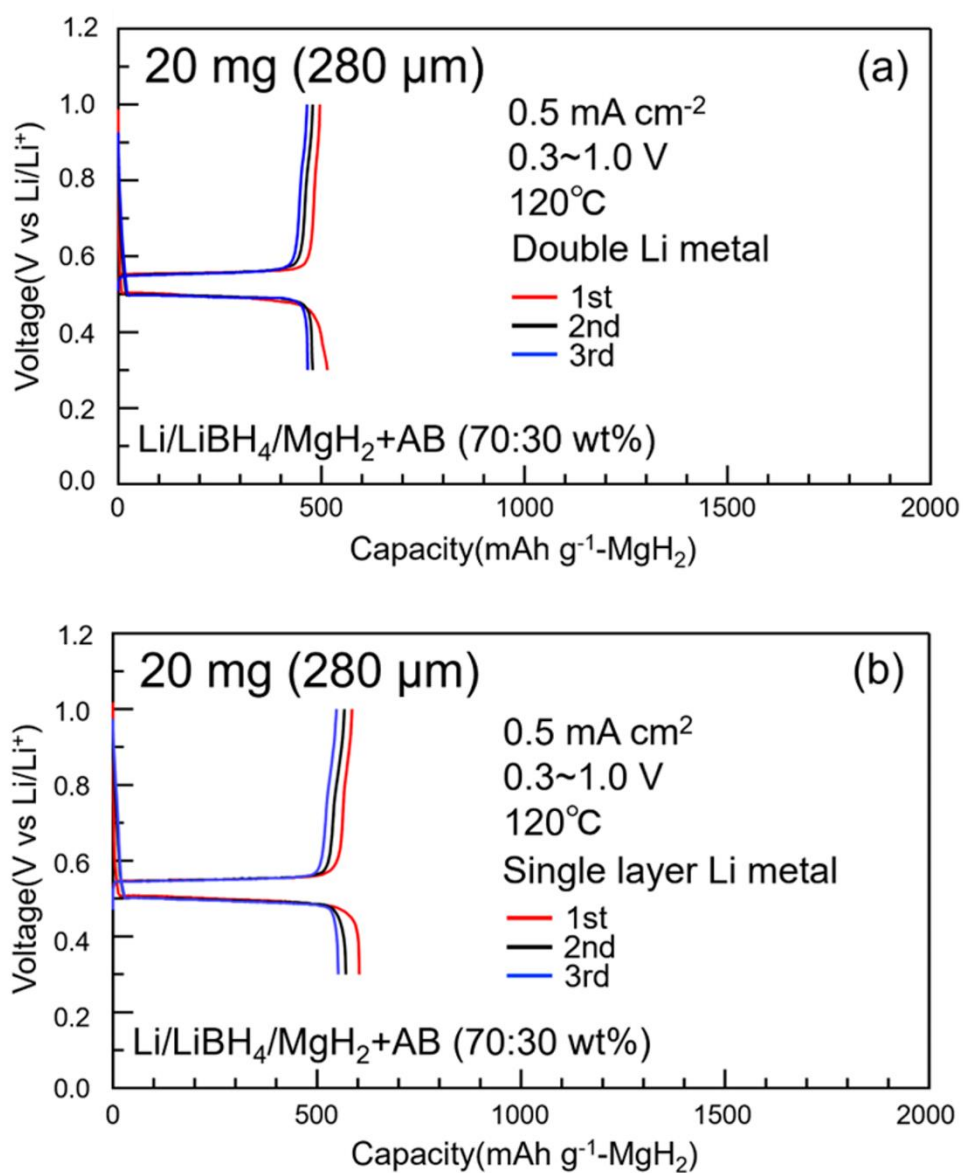


Figure 3-6. Charge–discharge voltage profiles of a 280 μm-thick MgH₂–AB electrode in a cell with a (a) double-thick and (b) single-thick Li counter electrode.

I conducted *ex situ* XPS measurements to investigate the reaction distribution in the 84 and 280 μm -thick MgH_2 –AB electrodes (Fig. 3-7). For electrodes in the lithiated state, measured samples were collected from the electrode surface (current-collector side) and the entire electrode (by ball-milling the whole electrode). A sharp Mg 2s peak was observed at 90.4 eV in the XPS spectrum corresponding to the initial state; this peak is assigned to MgH_2 .^[18] After charge, for the 280 μm -thick electrode, no shift was observed in the Mg 2s peak compared with its position in the spectrum corresponding to the initial state, indicating that the MgH_2 at the surface (near the current collector) of the 280 μm -thick electrode did not react with Li^+ ions during charge. The main peak observed in the spectrum of the surface of the lithiated 84 μm -thick electrode shifted toward the low-binding-energy side to 88.4 eV, which is a peak position corresponding to metallic Mg;^[18,19] these results suggest that the MgH_2 active material in the current-collector side of the 84 μm -thick electrode also reacted with Li^+ ions.

I separated the electrode layer from the charged cells (LiBH_4 from electrolyte layer was also included) and ground the electrode pellets into powders by hand-milling to distribute the reacted and unreacted parts evenly. This procedure enabled us to investigate the mixed chemical state of the entire electrode using XPS. For the 280 μm -thick electrode, compared with the Mg 2s peak in the spectrum of the electrode surface, the characteristic

Mg 2s peak was observed at a lower-energy position because metallic Mg was also contained in the powders as the reaction product. The difference in chemical state indicates that the lithiation of MgH_2 was dominant in the shallow-depth region (calculated from the solid electrolyte layer) when the 280 μm -thick electrode was used. Powders of the 84 μm -thick electrode were prepared using the same method; however, no difference was observed between the peaks in the XPS spectra of the 6 mg electrode powders and those in the spectra of the electrode surface. These results suggest that the electrode reaction extended to the entire electrode layer because of the low electrode mass loading (thin electrode layer).

To investigate the position where Li extraction occurred during the delithiation process, I carried out XPS measurements of the current-collector side and the entire electrode in the 500 mAh g^{-1} delithiated state (84 μm -thick MgH_2 -AB electrode). The Mg 2s peaks corresponding to the current-collector side and entire electrode appeared at 90.2 eV (90.4 eV: MgH_2) and 88.9 eV (88.4 eV: Mg), respectively. These results indicated that the Li extraction preferentially occurred from the current-collector side and the Li^+ -ion conduction pathway was also maintained during the delithiation process, consistent with the high reversibility of the batteries.

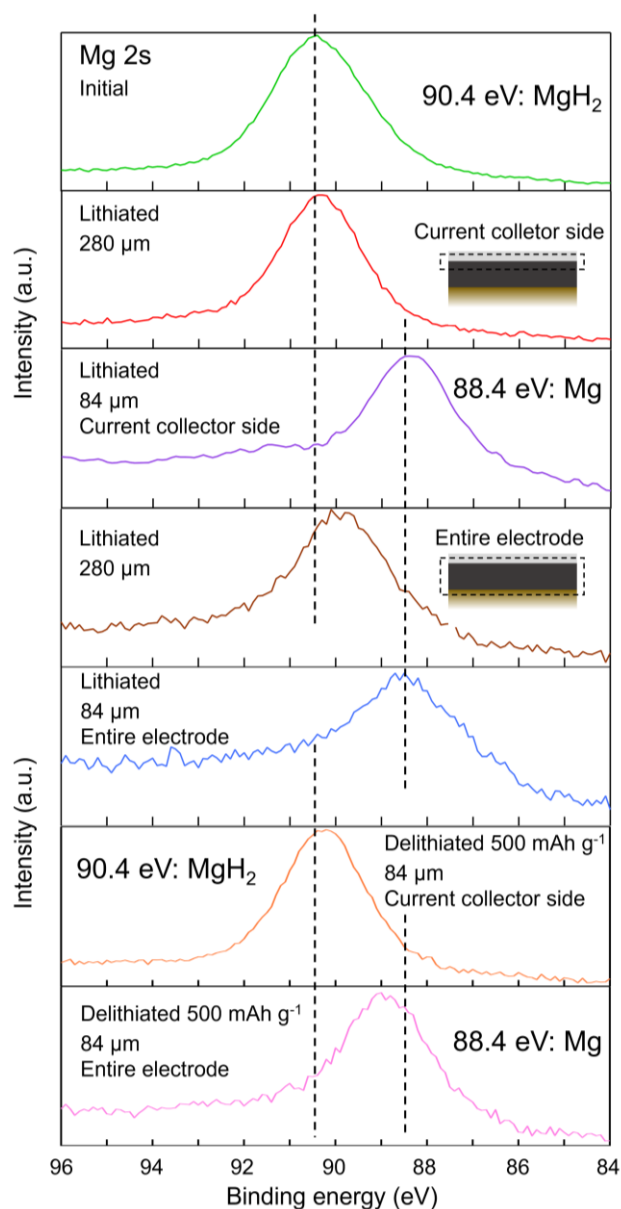


Figure 3-7. *Ex situ* Mg 2s XPS spectra of entire electrodes and current-collector sides of 6 and 20 mg MgH₂:AB (70:30 wt.%) composite electrodes.

To further investigate the distribution of the electrode reaction in a thick electrode, I carried out cross-sectional XPS measurements (Li 1s, Mg 2p, and Mg 2s) of a lithiated 30 mg electrode (Fig. 3-8). In addition, 11 positions in the cross section of the electrode layer from the current-collector side (A1)

to the solid electrolyte side (A11) were characterized using an X-ray beam (diameter: 110 μm). A cross-sectional image was also obtained using an optical microscope incorporated into the XPS instrument (Fig. 3-9). The electrode thickness is 300 μm (not the calculated 420 μm) because the part closest to the current collector has already separated from the lithiated electrode after removing the electrode from lithiated cell, resulting in a reduced measured electrode thickness. The Mg 2s spectra were exhibited in Fig. 3-8(a). For the point A1 and A2 corresponding to the current-collector side, peaks of MgH_2 at 90 eV can be observed. From point A3 to point A8, the Mg 2s peak shifts toward lower binding energies, indicating that the amount of metallic Mg measured increases toward the solid-electrolyte side. At points A9, A10, and A11, no peak shifts are observed, indicating the presence of metallic Mg (88.3 eV). These results are highly consistent with the results exhibited in Fig. 3-7. The Li 1s and Mg 2p spectra (Fig. 3-8(b)) reveal a gradual increase in the intensity ratio of the peaks as the point of analysis approaches the solid-electrolyte side (Fig. 3-10), indicating an increased content of Li atoms near the electrolyte layer. The decreased intensity of peaks at point A6 was considered as a result of an insufficient preheating time for the X-ray photoelectron spectrometer. For the Li 1s spectra (Fig. 3-8(b)), at point A9, the Li 1s peak shifted to 54.7 eV, which agreed with the previous reported value of LiH ,^[20] indicating the formation

of LiH, However, the weak peaks of Li 1s spectra were also observed at point A1 and A2, indicating Li atoms also existed near the current collector side. The existed Li atom in the current-collector side was tentatively attributed to the reaction between Li and a small amount of MgH_2 near the current collector. The Li 1s peaks appeared at 56.2 eV, consistent with the Li 1s peak positions reported for Li_2O ,^[21] suggesting that the Li atoms in the current-collector side were oxidized. O 1s peaks are also observed in the XPS survey spectra (Fig. 3-11). Compared with the entire electrode, a higher intensity of O 1s peak was observed in the current-collector side (lithiated 280 μm -thick electrode), indicating stronger oxidation in the current-collector side. I will strive to reduce the extent of oxygen contamination in samples in future research. In addition, because LiBH_4 was also detected in the electrolyte layer, the Li 1s peaks in the spectrum corresponding to point A9 and A11 shifted toward higher binding energies. In the Mg 2p spectra, MgH_2 peaks (51.1 eV) were observed at points A1 and A2 and then Mg peaks (49.4 eV) appeared at point A9,^[19,22] consistent with the Mg 2s spectra. Collectively, these results indicate that the electrode reaction occurs almost exclusively below a certain height (the reacted electrode thickness calculated by XPS measurement was 90–140 μm) above the electrolyte layer (with the possibility that a small amount of MgH_2 near the current-collector side reacts with Li), when the electrode is sufficiently thick. However, the reason for the

limitation of the reacted electrode thickness is unclear.

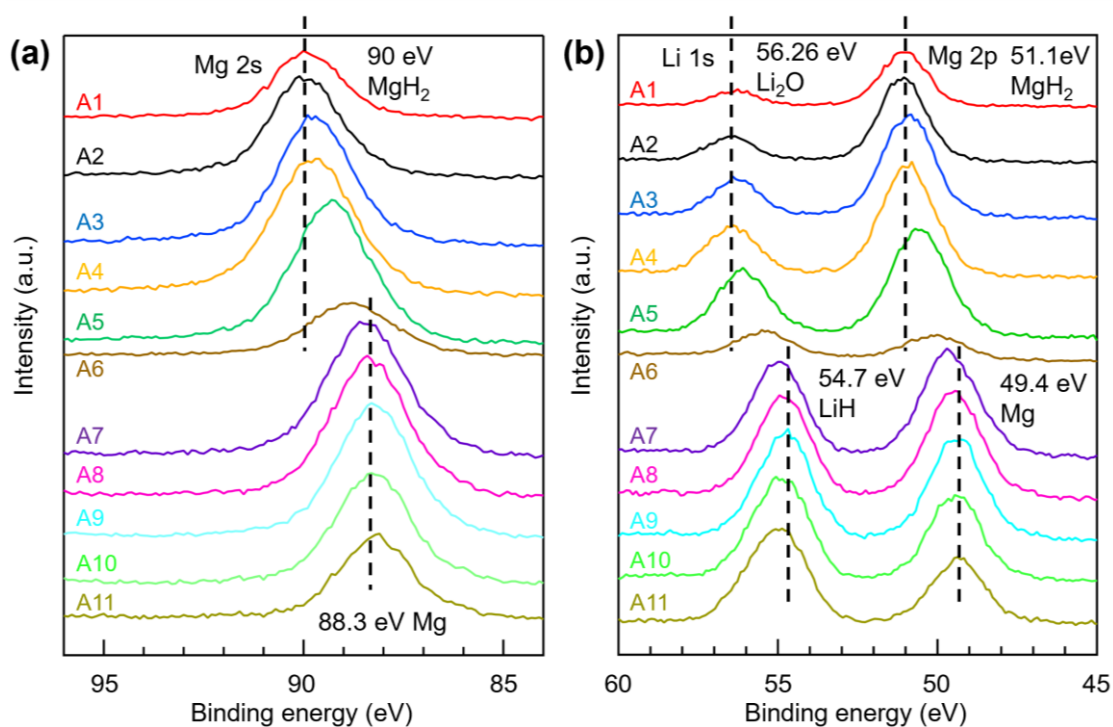


Figure 3-8. The cross-sectional XPS measurements of (a) Mg 2s and Li 1s and (b) Mg 2p spectra for the lithiated 30 mg MgH_2 -AB electrode (A1: current-collector side, A11: solid-electrolyte-layer side). After each measurement, the measurement position was moved 30 μm ; the diameter of the X-ray beam was 110 μm .

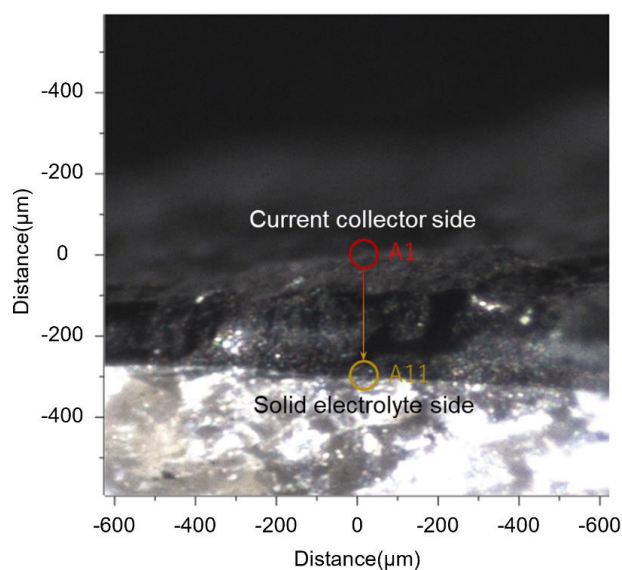


Figure 3-9. Cross-sectional image of a lithiated 30 mg MgH_2 -AB electrode.

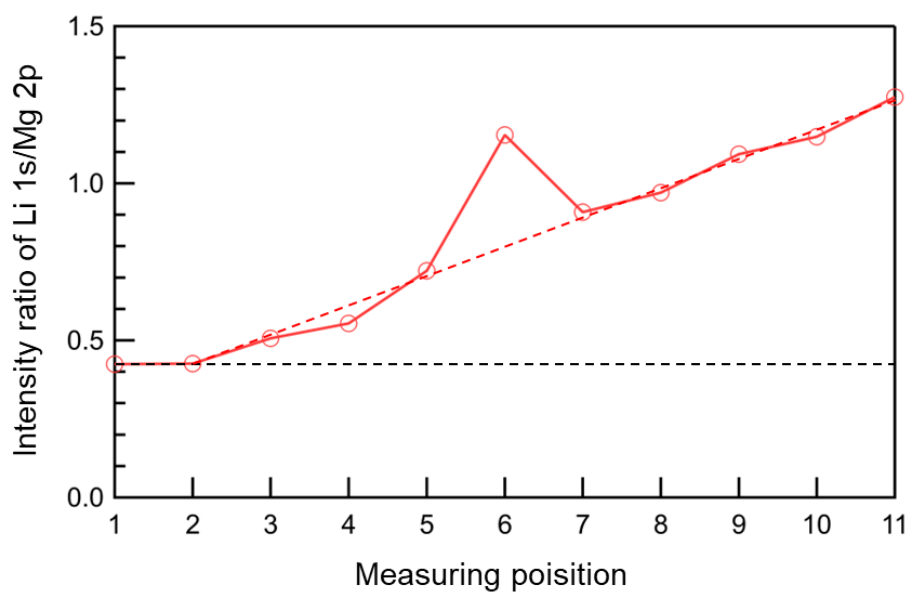


Figure 3-10. Intensity ratio of Li 1s/Mg 2p.

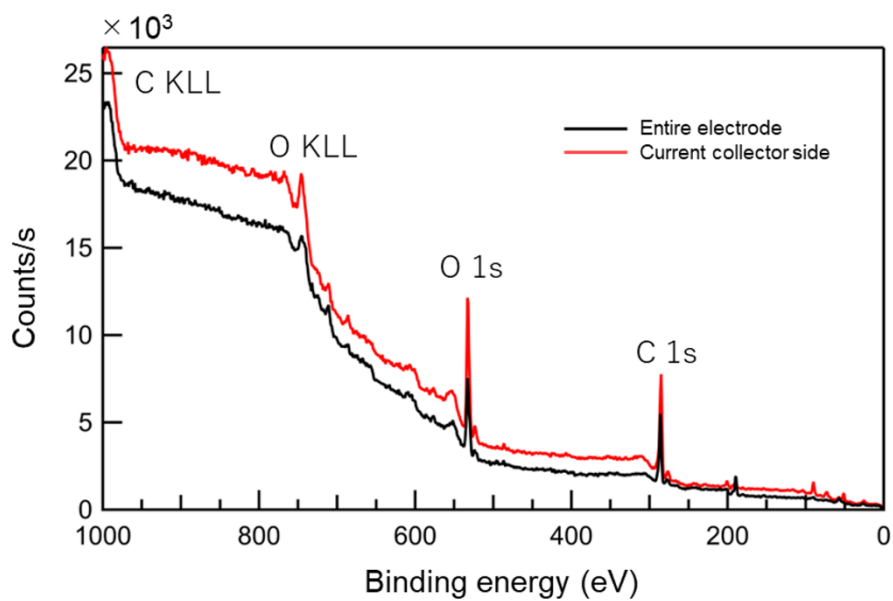


Figure 3-11. *Ex situ* XPS survey spectra of a lithiated 280 μm -thick MgH_2 -AB electrode.

A comparison of the lithiated gravimetric capacity (mAh g^{-1}) and lithiated areal capacity (mAh cm^{-2}) of 63, 84, 140, 280, and 420 μm -thick (4.5, 6, 10,

20, and 30 mg) MgH₂–AB electrodes is presented in Fig. 3-12. For comparison, the results for Ca(BH₄)₂–AB (70:30 wt%) and Mg(BH₄)₂–AB (70:30 wt%) (charge–discharge curves are shown in Fig. 3-13) with different anode mass loadings are also presented. For the MgH₂–AB electrode, when the electrode is less than 140 μm thick (10 mg), the areal capacity improves from 6.3 to 8.7 mAh cm⁻² because of the greater amount of active material. Meanwhile, the 140, 280, and 420 μm-thick (10, 20, and 30 mg) MgH₂–AB electrodes exhibit similar areal capacities of 11.03, 10.75, and 11.37 mAh cm⁻², respectively. This result indicates that the amount of MgH₂ active material that contributes to the battery capacity is almost constant when the electrode thickness exceeds 140 μm (10 mg). In addition, the reacted thickness of the MgH₂–AB electrode was calculated to be 110 μm on the basis of the initial charge capacity, which is consistent with the value obtained by XPS analysis. A substantial decrease in the initial lithiated capacity was not observed when Ca(BH₄)₂ and Mg(BH₄)₂ were used as the active material. Both of them achieved an importantly increased areal capacity due to thickened electrodes. These results are attributed to the high conductivity of LiBH₄ formed *in situ*. For the MgH₂–AB electrodes, I speculate that the low ionic conductivity of LiH makes the formation of a Li⁺-ion conduction pathway increasingly difficult with increasing depth until the Li⁺-ion conductivity becomes insufficient to support the lithiation

process. Because of the high active material content and thick electrodes, I achieved a greater areal capacity than was achieved in previous studies, even with the limitation of the Li^+ -ion conduction pathway.^[11,15] To investigate the influence of electronic conductivity on electrochemical performance of thickened electrode, the results of DC polarization measurement using $\text{MgH}_2\text{-AB}$ (50:50 wt%), $\text{MgH}_2\text{-AB}$ (70:30 wt%) and $\text{MgH}_2\text{-AB}$ (90:10 wt%) electrodes were exhibited in Fig. 3-14(a). From the results of DC polarization, the electronic conductivity of $\text{MgH}_2\text{-AB}$ (50:50 wt%), $\text{MgH}_2\text{-AB}$ (70:30 wt%) and $\text{MgH}_2\text{-AB}$ (90:10 wt%) is $7.0 \times 10^{-2} \text{ S cm}^{-1}$, $6.8 \times 10^{-2} \text{ S cm}^{-1}$ and $1.1 \times 10^{-6} \text{ S cm}^{-1}$, respectively. Although, the electronic conductivity of $\text{MgH}_2\text{-AB}$ electrode significantly improved after AB content was increased from 10 wt% to 30 wt%. Compared with $\text{MgH}_2\text{-AB}$ (70:30 wt%) electrode, a consistent value achieved when used $\text{MgH}_2\text{-AB}$ (50:50 wt%) electrode. It is suggested that 30 wt% AB may exceed the percolation limit and is enough to provide sufficient electronic conductivity. In addition, the electrochemical measurement of 20 mg $\text{MgH}_2\text{-AB}$ (50:50 wt%) electrode was also performed (Fig. 3-14(b)). Compared to 6 mg $\text{MgH}_2\text{-AB}$ (70:30 wt%) electrode, the capacity (643 mAh g^{-1}) also decreased dramatically, indicating the electronic conductivity of electrode may not play a crucial role in the limitation of reacted thickness.

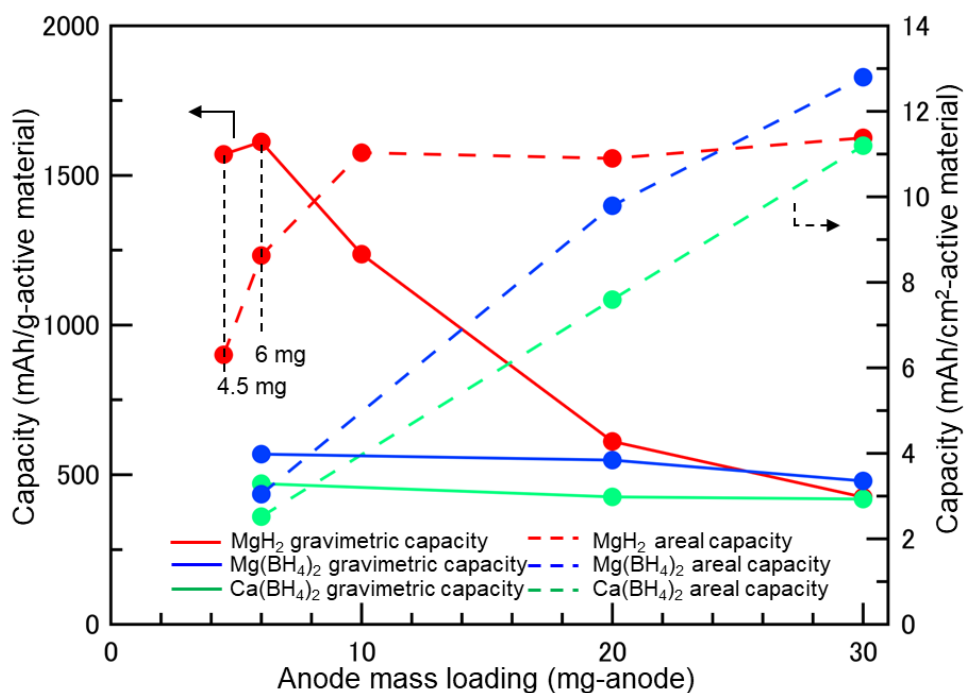


Figure 3-12. Comparison of the initial discharge capacity of different electrodes with various electrode thicknesses. Values reported for a metal hydride anode are shown for comparison.

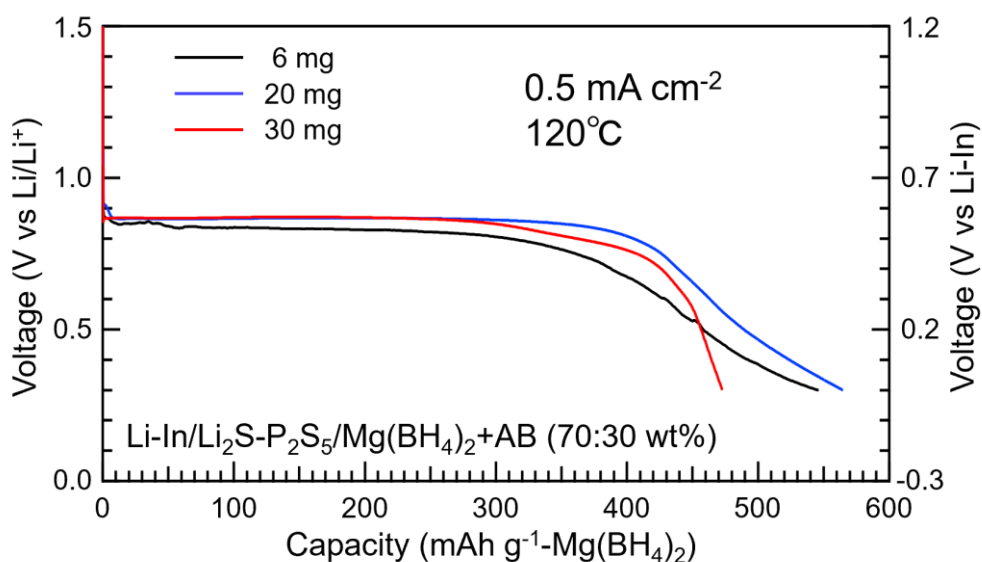


Figure 3-13. Charge-discharge voltage profiles of $\text{Mg}(\text{BH}_4)_2$ -AB electrodes with various electrode masses.

To confirm our hypothesis that an insufficient Li^+ -ion conduction pathway led to the decrease in capacity, I investigated the rate capability of the 20 mg MgH_2 electrodes with and without LiBH_4 added (Fig. 3-15). Figure 3-15(a) shows the initial charge profiles of the MgH_2 -AB electrodes at current densities of 0.1 and 0.5 mA cm^{-2} . Even when the current density was decreased from 0.5 to 0.1 mA cm^{-2} , the capacity improved by only 15 mAh g^{-1} . Compared with the MgH_2 -AB electrode, the MgH_2 - LiBH_4 -AB electrode showed a substantial improvement in charge capacity from 766 to 1240 mAh g^{-1} when the current density was reduced to 0.1 mA cm^{-2} even though the 20 mg MgH_2 - LiBH_4 -AB electrode (305 μm) was thicker than the 20 mg MgH_2 -AB electrode (280 μm). The faster kinetics of the thicker MgH_2 - LiBH_4 -AB electrode might be due to the rapid diffusion of Li^+ as a result of the addition of LiBH_4 to the electrode composite. Combined the results exhibited in Fig. 3-15 and Fig. 3-13 (charge-discharge measurement of $\text{Mg}(\text{BH}_4)_2$ -AB (70:30 wt%) electrode), it was suggested that the loss of Li^+ -ion conduction pathways in the 280 μm -thick MgH_2 -AB electrode composite was the main cause of the substantial amount of inactive MgH_2 , which led to the decrease in capacity. Therefore, the addition of an active material that forms an electrolyte with high ion conductivity and a high solid electrolyte/active material volume ratio is an effective method to improve

the charge–discharge performance of batteries with thick electrodes.

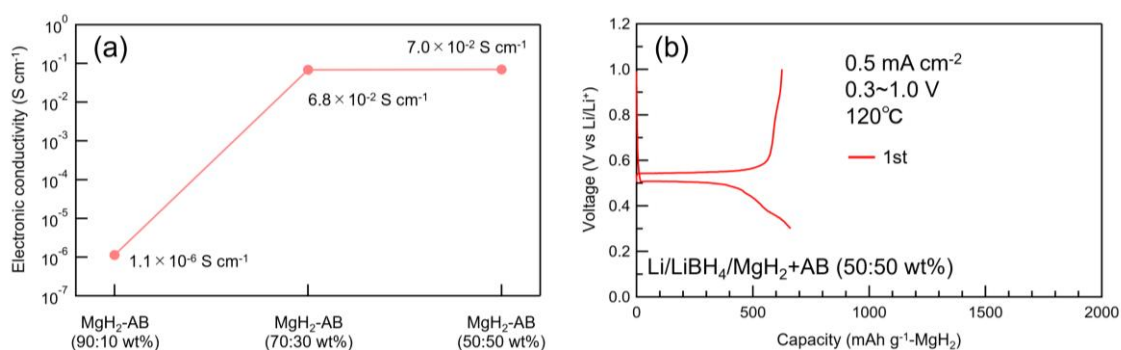


Figure 3-14. (a) Polarization current–time curves for electrodes under 0.1 V; (b) charge–discharge voltage profiles for 20 mg $\text{MgH}_2\text{-AB}$ (50:50 wt%) electrode.

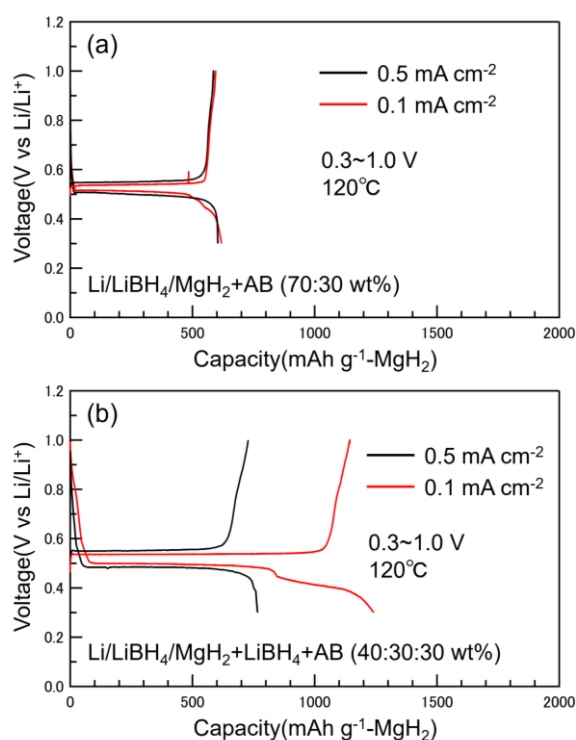


Figure 3-15. The rate capability of (a) a 20 mg (280 μm) $\text{MgH}_2\text{-AB}$ anode (70:30 wt%) and (b) a 20 mg (305 μm) $\text{MgH}_2\text{-LiBH}_4\text{-AB}$ anode (40:30:30 wt%) at different current densities of 0.5 and 0.1 mA cm^{-2} .

3.3 Conclusions

In this chapter, the correlation between charge–discharge performance and electrode thickness of an active material that forms a solid electrolyte *in situ* was discussed and the reaction mechanism was investigated. The results of experiments suggest that the energy density of these LIBs could be increased further without compromising the *in situ* electrolyte formation concept in some cases. For example, a $\text{Ca}(\text{BH}_4)_2$ battery with a thicker electrode (20 mg $\equiv$ 290 μm thickness) also cycled reversibly and showed comparable capacity to a battery with a thinner electrode (6 mg $\equiv$ 87 μm) in initial cycle. Areal capacity increased significantly due to thickened electrodes. However, the cells show a substantial decrease in initial charge capacity when a MgH_2 –AB electrode with a thickness from 84 μm (6 mg) to 420 μm (30 mg) is used. I found that a large amount of the MgH_2 active material does not contribute to the capacity because it is unable to react with Li^+ ions. In addition, the unreacted MgH_2 active material was investigated to be located near the current collector due to XPS analysis and the reacted electrode thickness was found to be limited to 90–140 μm . Nonetheless, further efforts are needed to improve the energy density of batteries based on MgH_2 anode.

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Chapter 4

Utilization of *In situ* Formation of Solid Electrolyte and Bifunctional material for High Volumetric Energy Density Electrode with Minimal Content of Conducting Agent

4.1 Introduction

In chapter 3, I tried to increase energy density by using thickened electrode, even $\text{Ca}(\text{BH}_4)_2$ electrode can perfectly adapted to this method. Capacity of MgH_2 decreased significantly with the increased electrode thickness. Therefore, it is necessary to improve the energy density of MgH_2 anode by other hands. From chapter 1, a MgH_2 -AB (AB = acetylene black) electrode composite without a solid electrolyte exhibited a capacity similar to that of a MgH_2 - LiBH_4 -AB electrode composite, even though the Li^+ -ion conductivity of LiH is as low as 10^{-7} S/cm at 120°C [1]. However, the content of the conductive agent remains at 30%, and the low-density carbon will still significantly limit the volumetric energy density of the battery. Reducing the

carbon content and further increasing the active material content will be beneficial for enhancing the energy density of the electrode. Like MgH_2 , it is possible that other metal hydrides can act as active materials that form solid electrolytes *in situ*.

Metal hydrides such as MgH_2 and TiH_2 have been intensely studied as conversion-type anode materials for ASSBs in which LiBH_4 is used as an electrolyte and which are operated at 120°C [2,3]. This interest in MgH_2 and TiH_2 stems from their high theoretical capacity and suitable working potentials [4-6]. Compared with MgH_2 , TiH_2 shows a theoretical capacity of 1074 mAh/g and a lower redox potential of 0.15 V vs. Li^+/Li [7,8]. From the viewpoint of increasing the voltage of a battery, TiH_2 is believed to enable the fabrication of higher-voltage batteries than MgH_2 because of its lower working potential. TiH_2 has also been reported to function as an electron conductor with a high conductivity of 10^4 S/cm at room temperature [9]. Furthermore, it exhibits a high density of 3.83 g/cm^3 and the largest volumetric capacity among metal hydrides [10]. In a previous study, a MgH_2 - TiH_2 nanocomposite was synthesized via reactive grinding of a $0.7\text{Mg} + 0.3\text{Ti}$ mixture under H_2 gas, which resulted in a metastable ternary Mg-Ti-H phase [11]. A $\text{MgH}_2 + \text{TiH}_2$ nanocomposite obtained by the same approach was used as an anode material in Li^+ -ion batteries [12-14]. In the present study, to avoid the formation of the Mg-Ti-H phase while taking advantage of the

high electronic conductivity and density of TiH_2 , I used MgH_2 , TiH_2 , and AB as starting materials to prepare electrode composites via a ball-milling method. Using TiH_2 as a bifunctional active material-electronic conductor material, and replacement for carbon additives in electrode composites is considered a feasible strategy for increasing composite electrodes' active material content. This approach also improves the volumetric energy density of the electrode composites compared with that of electrodes prepared with large amounts of low-density carbon additives.

This work aims to investigate the electrochemical properties of TiH_2 -AB electrode composites without a solid electrolyte and to exploit the ability of TiH_2 to form an electrolyte *in situ* to increase the capacity of batteries. The high electronic conductivity and density of TiH_2 are exploited to fabricate ASSBs based on $x\text{MgH}_2-(1-x)\text{TiH}_2$ -AB electrode composites; the resultant ASSBs have increased active material contents and high volumetric energy densities. In addition, combining the *in situ* solid-electrolyte formation mechanism of both the MgH_2 and TiH_2 active materials enables the unneeded solid electrolyte material to be omitted and further increases the content of active material in the electrode. The reaction mechanisms for the TiH_2 -AB and $x\text{MgH}_2-(1-x)\text{TiH}_2$ -AB electrode composites were also clarified by X-ray diffraction (XRD) measurements and electrochemical methods. For comparison, the electrochemical performance of an electrode composite

blended with vapor-grown carbon fiber (VGCF) as a carbon additive was also investigated; the composite exhibited a high specific capacity of 1342 mAh/g with a high active material content of 90 wt% in electrode.

4.2 Experimental

4.2.1. Materials synthesis

The TiH₂-AB electrode (sample 1) composite with no solid electrolyte was prepared from commercial TiH₂ powder (95%, Sigma-Aldrich) and AB (97%, Denka) in a mass ratio of 70:30 by ball-milling under an Ar atmosphere. The TiH₂ active material was loaded into a zirconia milling jar together with AB in a weight ratio of 70:30; the total amount was 500 mg with 20 g of ZrO₂ balls (diameter: 3 mm). The mixtures were milled for 30 min at a rotation speed of 400 rpm. For comparison, an electrode composite with a solid electrolyte was prepared with TiH₂, LiBH₄ (95%, Wako), and AB with a mass ratio of 40:30:30. The same milling conditions used for the TiH₂-AB electrode composite were also used for the TiH₂-LiBH₄-AB electrode composite (sample 2). To investigate whether the electronic conductivity of TiH₂ was sufficient for the AB content in the electrode composite to be reduced, I also prepared TiH₂-AB (90:10 wt%) (sample 3) and TiH₂ (100 wt%) (sample 4) under the same milling conditions previously

described. To increase the content of active material and improve the volumetric energy density of batteries, TiH_2 was blended with MgH_2 (95%, Wako) as a conductor additive and active material. MgH_2 powder, TiH_2 powder, and AB were loaded into a milling pot with a mass ratio of 63:27:10 wt% (MT73AB10), 45:45:10 wt% (MT55AB10), or 27:63:10 wt% (MT37AB10). The rotation conditions for ball-milling were fixed at 400 rpm and 30 min, which were the same conditions used for the TiH_2 electrode composites. The MgH_2 - TiH_2 -VGCF (45:45:10 wt%) (MT55VG10) was also fabricated under the same ball-milling conditions to enable a comparison of the carbon materials. The weight ratio and abbreviation of main electrode composites were exhibited in Table 4-1.

4.2.2. Half cells assembly

For the assembly of Li metal/ LiBH_4 / TiH_2 -AB and MgH_2 - TiH_2 -AB (VGCF) electrode batteries, a Li-foil disk was pressed by hand onto a stainless-steel plate (SUS), 60 mg of LiBH_4 was added as the electrolyte, and the mixture was compacted at 255 MPa. The electrode composite was placed on top of the electrolyte layer with a load of 6 mg and was pressed at 318 MPa to complete the half-cell. A SUS plate with a diameter of 10 mm was used as the current collector.

4.2.3. Electrochemical measurements and Characterization

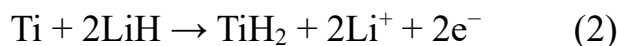
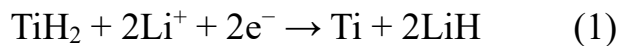
Galvanostatic charge-discharge and galvanostatic intermittent titration technique (GITT) measurements on these cells were conducted at 120°C, which was above the phase-transition temperature of LiBH₄. 2.16 C (0.6 mAh) were loaded each charge-discharge process at 0.3 mA cm⁻² with a relaxation time of 8 h, using a battery tester (Hokuto Denko, HJ1020mSD8). Electrochemical impedance spectroscopy (EIS) measurements were performed on an electrochemical workstation (Biologic, VSP) in the frequency range from 100 mHz to 1 MHz at an amplitude of 10 mV. *Ex situ* XRD measurements (Rigaku RINT-TTRIII) were performed at different stages of the charge-discharge process to clarify the reaction mechanism for the TiH₂ and the MgH₂-TiH₂ electrode composite.

4.3 Results and Discussion

4.3.1. Conversion reaction of TiH₂

Charge-discharge experiments on the TiH₂ electrodes with and without additional electrolyte were performed to investigate the performance of *in situ*-formed LiH as an electrolyte. The charge-discharge profiles for the TiH₂-LiBH₄-AB electrode composite (sample 1) exhibit a plateau at ~0.15 V in the discharge (lithiation) process (including the lithiation of TiH₂ to form fcc TiH_{1.5} and fcc TiH; and further lithiation of fcc TiH_{1.5} and fcc TiH to form

Ti) and charge (delithiation) plateau at ~0.2 V, consistent with previously reported data (Fig. 4-1(a)).^[7,8] The two plateaus can be regarded as the result of a conversion reaction expressed as



In addition, sample **1** reached a specific discharge capacity of 1100 mAh/g, indicating that the active material was completely reacted with Li^+ . The capacity exceeded the theoretical capacity (1074 mAh/g), which I tentatively attributed to Li insertion into AB ^[7]. For the TiH_2 -AB electrode without electrolyte (sample **2**) (Fig. 4-1(b)), a comparable initial discharge capacity (1201 mAh/g) was achieved even without LiBH_4 in the electrode composite. This finding suggests that the *in situ* formation of LiH is sufficient to provide an ionic conduction pathway during the lithiation process. Notably, the actual capacity of TiH_2 cells is displayed on the upper axis of Fig. 4-1(a, b), where sample **2** exhibits a higher actual capacity than sample **1** because of the increased active material content. The cycle performance of samples **1** and **2** (Fig. 4-1(e, f)) is approximately the same. However, in the first discharge curve for the TiH_2 -AB electrode, a plateau appeared at ~0.12 V below the redox voltage of the TiH_2 active material. Obviously, TiH_2 can be regarded as a new solid electrolyte formed *in situ* as an active material, leading to

successful charge-discharge in the absence of a solid electrolyte in the electrode composite.

Table 4-1. The weight ratio and abbreviation of main electrode composites.

Electrode composite	TiH ₂ -LiBH ₄ -AB	TiH ₂ -AB	TiH ₂ -AB	TiH ₂	MgH ₂ -AB	MgH ₂ -TiH ₂ -AB	MgH ₂ -TiH ₂ -AB	MgH ₂ -TiH ₂ -AB	MgH ₂ -TiH ₂ -VGCF
Weight ratio	40:30:30	70:30	90:10	100	90:10	27:63:10	45:45:10	63:27:10	45:45:10
Sample name	Sample 1	Sample 2	Sample 3	Sample 4	M10AB10	MT73AB10	MT55AB10	MT37AB10	MT55VG10

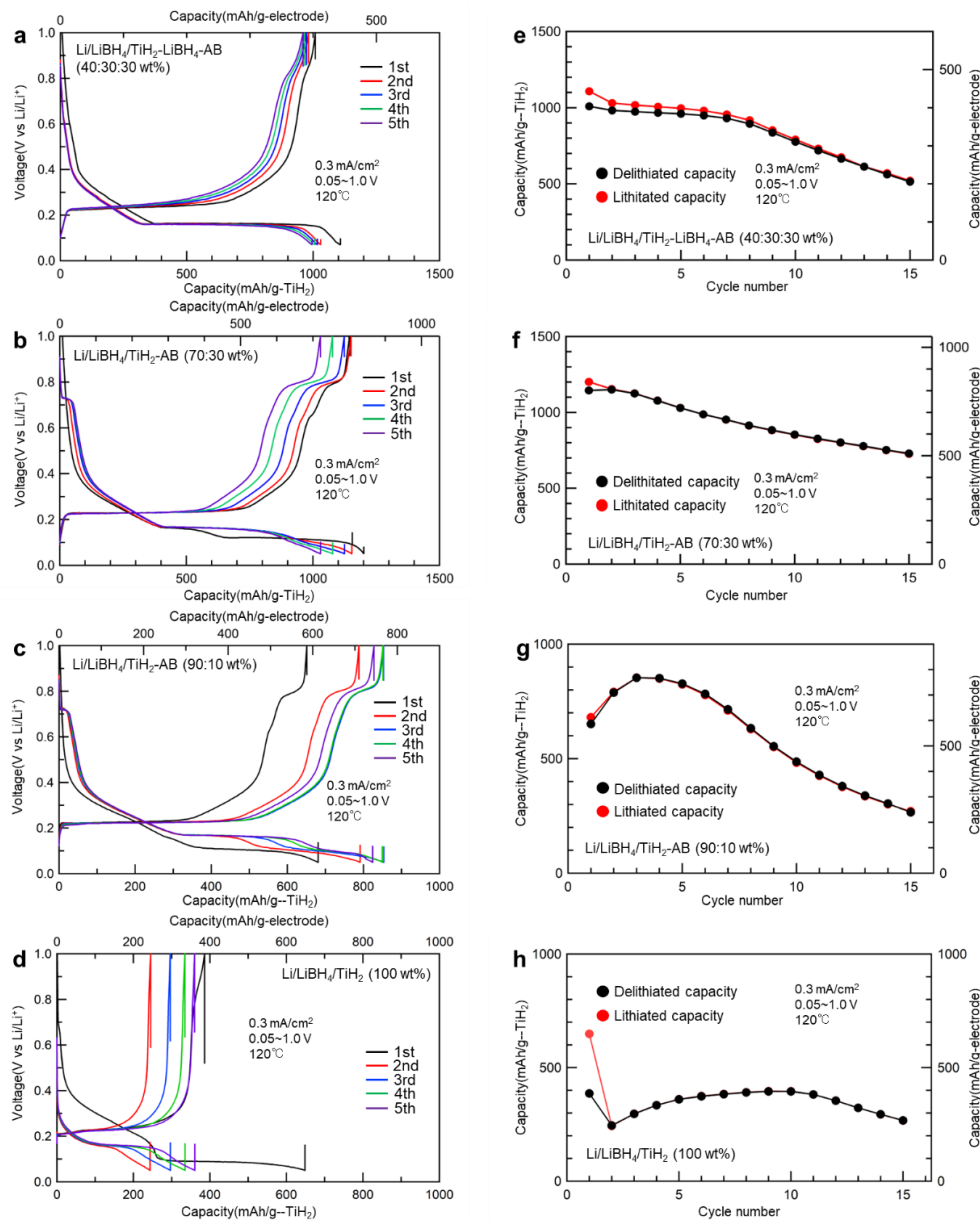


Figure 4-1. (a) Charge–discharge profiles for sample 1 (TiH₂:LiBH₄:AB = 40:30:30 wt%); (b) charge–discharge profiles for sample 2 (TiH₂:AB = 70:30 wt%); (c) charge–discharge profiles for sample 3 (TiH₂:AB = 90:10 wt%); (d) charge–discharge profiles for sample 4 (TiH₂ = 100 wt%) and (e, f, g, h) cyclabilities of samples 1, 2, 3 and 4, respectively.

An XRD analysis was performed to clarify the reaction products of sample **2** in different charge-discharge states (Fig. 4-2, Initial: the state before charge-discharge measurement, Lithiated 1: the state when the cell was lithiated to 0.12 V, Lithiated 2: the state when the cell was lithiated to 0.05 V, Delithiated: the state when the cell was delithiated to 1.0 V). In the XRD pattern corresponding to the initial state, only diffraction peaks associated with TiH_2 were observed. In the pattern for the sample in the lithiated state before the plateau at ~ 0.12 V (Lithiated **1**), the peaks due to TiH_2 disappeared and peaks corresponding to face-centered cubic (fcc) TiH_{2-x} ($\text{TiH}_{1.5}$) and face-centered orthorhombic (fco) TiH were observed, suggesting that the reaction between Li and TiH_2 led to the partial extraction of H from TiH_2 . After further lithiation to 0.05 V (Lithiated **2**), mainly metal Ti peaks were observed in the XRD pattern. Hence, the plateau at 0.12 V is attributed to Li insertion into the fcc TiH_{2-x} and fco TiH rather than to a side reaction. The electrode reaction for TiH_2 -AB is consistent with that for the TiH_2 - LiBH_4 -AB electrode reported in a previous study.^[8] In the pattern for the sample in the delithiated state, the peaks corresponding to TiH_2 reappeared, consistent with the results of charge-discharge measurements, indicating that sample **2** also demonstrates high reversibility even without the addition of a solid electrolyte in the electrode composite.

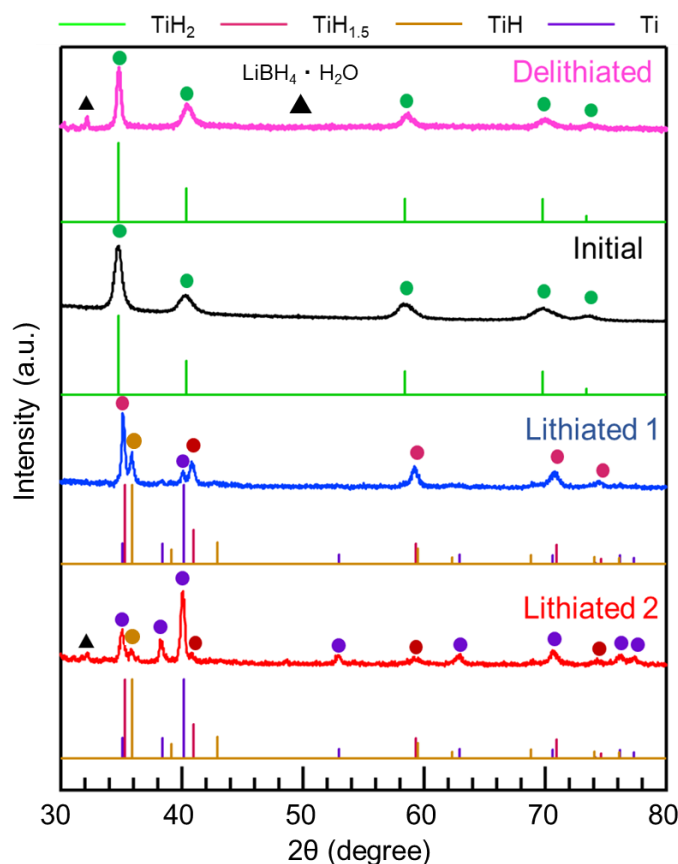


Figure 4-2. Comparison of *ex situ* XRD patterns before and after the initial charge–discharge cycles for TiH₂–AB (70:30 wt%) composite electrode. Patterns generated from structures of possible products within the ICSD are shown for reference. (TiH₂ ICSD: 638505, TiH_{1.5} ICSD: 63427, TiH ICSD: 56181, Ti ICSD: 76265)

GITT measurements (Fig. 4-3) were performed to further investigate the reaction mechanism of the sample **2** electrode composite. In the GITT curve corresponding to the first cycle, two plateaus at ~ 0.15 and ~ 0.12 V were observed in the lithiation process. However, the plateau at ~ 0.12 V disappeared and only one plateau was observed at ~ 0.15 V in the curve corresponding to the lithiation process in the second cycle. The GITT measurements indicate that, in the latter lithiation process (600-1200 mAh/g), an increased polarization from 600 mAh/g and almost the same polarization

were obtained in the first and second cycle, respectively. These results indicate that the decrease in reaction potential from 0.15 V to 0.12 V is primarily caused by the increased polarization. This high polarization was weakened in the second cycle because of the close contact between the active material and the solid electrolyte. For the further investigation, the EIS measurement was performed on sample 2 during lithiation process (Fig. 4-4). From the results of Fig. 4-4, compared with the 1st half lithiation (600 mAh/g), 2nd half lithiation (600 mAh/g) exhibited a decreased charge transfer resistance, which is consistent with the low polarization of 2nd cycle. In addition, decreased bulk resistance of the cell (intercept of the x-axis) can also be considered as the result of *in situ* formed electrolyte. These results show that the reaction mechanism for the TiH_2 -AB electrode is identical to that for the traditional TiH_2 - LiBH_4 -AB electrode.

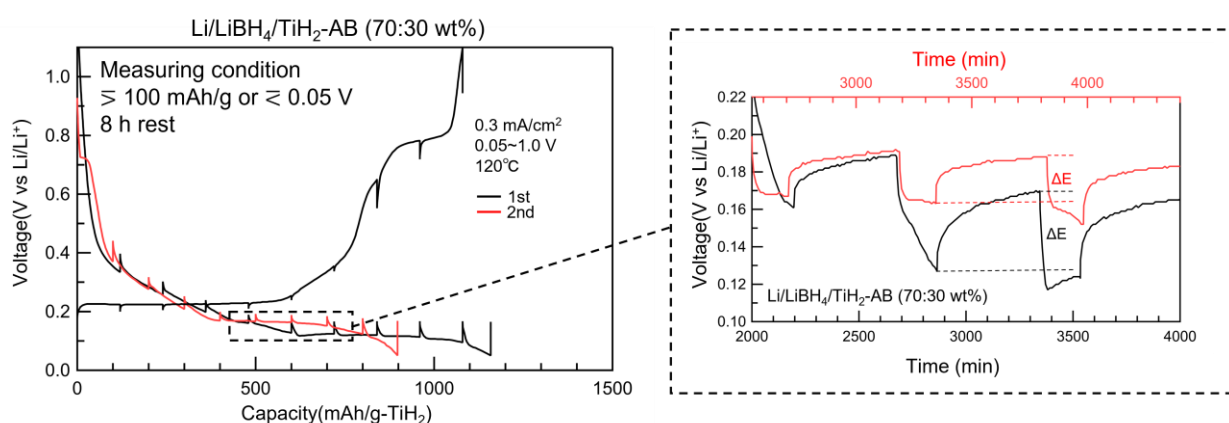


Figure 4-3. GITT profiles for TiH_2 -AB composite electrode (2.16 C (0.6 mAh) were loaded each charge-discharge process at 0.3 mA cm^{-2} with a relaxation time of 8 h).

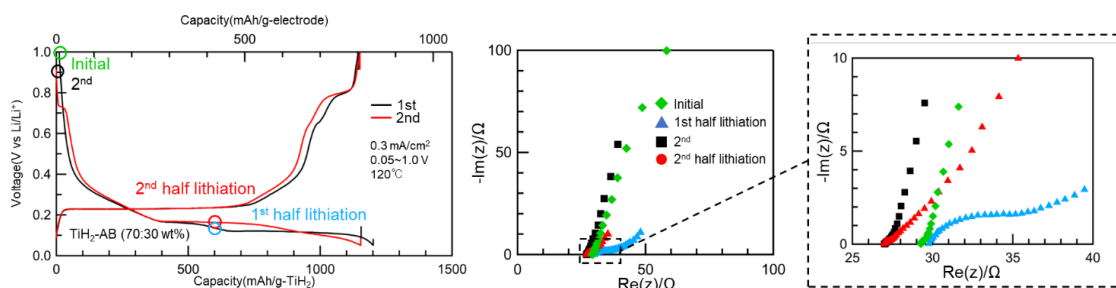


Figure 4-4. Charge-discharge profiles and EIS plots for TiH_2 -AB electrode (70:30 wt%). The right graphs is the enlarged view of the areas enclosed by dotted lines in the center graph.

To maximize the utilization of the high electronic conductivity and *in situ*-formed LiH, I fabricated cells using TiH_2 -AB (90:10 wt%) (sample **3**) and TiH_2 (100 wt%) (sample **4**) electrode composites with extremely high active material contents. Sample **3** demonstrated successful operation even with a small amount of added carbon conductor, yielding an initial discharge capacity of 681 mAh/g (Fig. 4-1(c)). Strikingly, for the TiH_2 (100 wt%) electrode, an initial lithiation capacity of 649 mAh/g was observed even without a conductor additive (Fig. 4-1(d)). This result indicates that the *in situ*-formed LiH and high electronic conductivity of the TiH_2 provide sufficient conduction pathways for the electrode composite to function without a conductor additive. The XRD patterns for TiH_2 (100 wt%) (Fig. 4-5) show peaks assigned to $\text{TiH}_{1.5}$, TiH , and metallic Ti, suggesting that no side reaction occurred, indicating the plateau at a low voltage during the first cycle is attributable to high polarization. In the second cycle, a new plateau

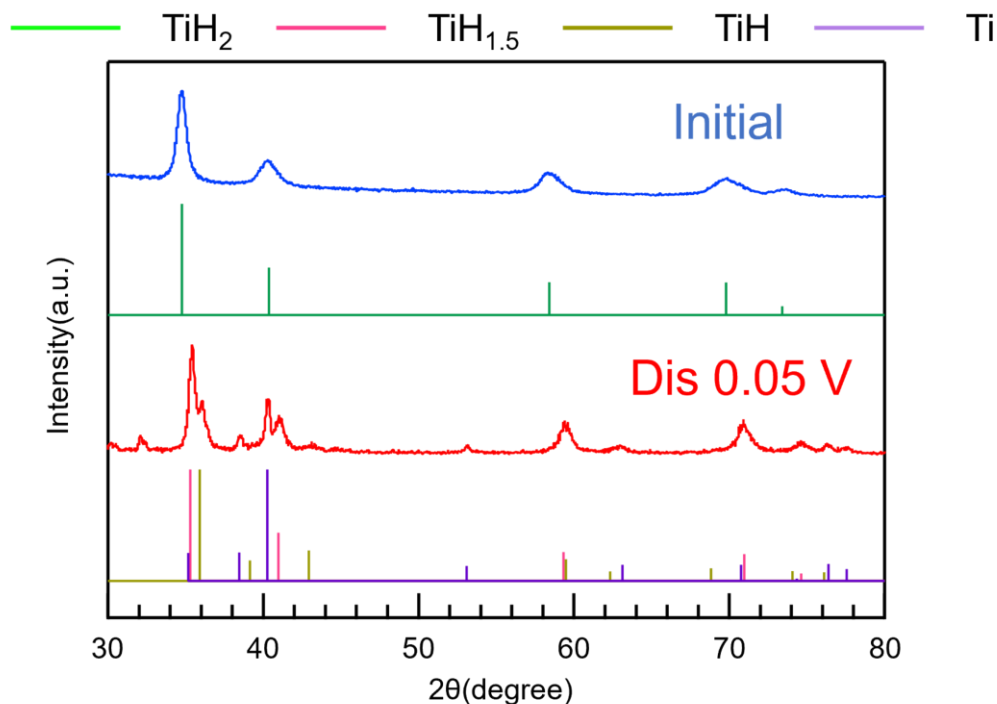


Figure 4-5. XRD profiles for initial and lithiated states down to 0.05 V vs. Li for TiH_2 (100 wt%) electrode composite.

emerged at 0.15 V, in good agreement with the results for sample **2**. Regarding the cycling performance (Fig. 4-1(g, h)), the discharge-charge capacity increased with increasing cycle number for the batteries. This result is identical to that in our previous study of MgH_2 ,^[15] indicating the gradual connection of ionic and electronic conduction pathways during battery cycling. Compared with sample **2** (the initial specific capacity: 1201 mAh/g), sample **3** and sample **4** exhibited the lower specific capacity of 853 mAh/g (3rd cycle) and 649 mAh/g (1st cycle) due to the relatively low AB content, indicating the maximized utilization ratio of TiH_2 active material can be achieved by sample **2**. However, when comparing actual capacity (calculated by weight of anode), a smaller difference between capacities can be achieved

for sample 2 (840 mAh/g), sample 3 (768 mAh/g) and sample 4 (649 mAh/g) because of improved content of active material. From the prospect of volumetric capacity, which will be discussed in the following article, the value of sample 3 exceed sample 2, indicating the advantage of low AB content of electrode.

For the sample 1, sample 2 and sample 3, all of them exhibited a high coulombic efficiency indicating the high reversibility. However, sample 4 exhibited a large irreversible capacity in the first cycle. Compared with the initial state, the *in situ*-formed LiH (electronic insulator) and decreased amount of TiH₂ (electronic conductor) in the lithiated state likely inhibit electron transfer and cause low resistivity. A short plateau appeared at 0.8 V in the charging curve for the electrode composite including AB but not in the curve for the electrode prepared using only TiH₂. This plateau was also detected in a previous study in which MgH₂ or TiH₂ was used as an active material; I assumed that this plateau is caused by a reversible reaction between AB and the active materials.^[6,7,13] The plateau that appeared at 0.73 V in the second discharge curve (Fig. 4-1(a, b, c)) is attributed to the reverse reaction. Collectively, these results indicate that a high capacity can be attained using a TiH₂ electrode composite with low AB content (10 wt%, 0 wt%) even under high polarization, suggesting the possibility that TiH₂ can be substituted for an electronic conductor.

4.3.2. Effects of introducing TiH₂ to MgH₂-AB composite anode

To increase the capacity of batteries, both the solid electrolyte and the electron conductor should be replaced to improve the active material loading. Given the high conductivity of TiH₂ and the charge-discharge results for samples **3** and **4**, I speculated that TiH₂ can be used as both an active material and electron conductor to increase the energy density of batteries. In addition, TiH₂ is denser than carbon additives such as AB and VGCF, and the volumetric energy density of batteries would therefore be improved simultaneously. MgH₂ active material exhibits a high theoretical capacity of 2036 mAh/g (TiH₂ theoretical capacity: 1074 mAh/g). Compared with TiH₂ active material, an increased capacity can be achieved by mixing MgH₂ and TiH₂. XRD patterns for the different MgH₂-TiH₂-AB initial electrode composites are shown in Fig. 4-6. Only peaks corresponding to MgH₂ and TiH₂ are observed, indicating no impurity formed during the ball-milling process. The intensity of the MgH₂ peaks decreased with decreasing weight ratio of MgH₂.

DC polarization experiments were performed for different electrodes to evaluate the electronic conductivity of the different electrode composites (Fig. 4-7(a)). With increasing TiH₂ content, the electronic conductivity of the electrodes clearly improved compared with that of the MgH₂-AB (90:10 wt%) mixture. Fig. 4-7(b) shows charge-discharge curves for the Li/MgH₂-

TiH₂-AB and MgH₂-AB cells with weight ratios of 63:27:10 wt% (MT73AB10), 45:45:10 wt% (MT55AB10), 27:63:10 wt% (MT37AB10) and 90:10 wt% (M10AB10). The dotted lines in the Fig. 4-7(b) represent the theoretical capacity of each electrode. For MT73AB10, MT55AB10, and MT37AB10, due to the enough electric conducted pathways supplied by *in situ* formed LiH, TiH₂ and AB, high reversibility (coulombic efficiency: MT73AB10: 98%, MT55AB10: 97%, MT37AB10: 97%) achieved. The high reversibility of MgH₂-TiH₂-AB electrodes indicates the *in situ* formed LiH can supply enough Li-ion conduction pathway for each solid electrolyte *in situ* formed active material. This result is beneficial for us to expand more combination between solid electrolyte *in situ* formed active materials in the future study. Initial discharge capacities of 1171, 1097, and 985 mAh/g were obtained, which correspond to electrode utilization ratios of 67%, 70%, and 72% (Fig. 4-7(c)), respectively. These results suggest that the increased electronic conductivity provided by the high content of TiH₂ can promote dynamic electrode reactions. It was preliminarily thought that the observed reduction in capacity corresponding to TiH₂ during cycling is predominantly attributed to the volume change of TiH₂ active material (the theoretical volume expansion, calculated based on the equation 1, is 229%). Due to the high reversibility of MgH₂-TiH₂-AB electrodes, I thought that only few parts of LiH might be broken during charge-discharge process by volume change

even LiH is a weak strength compound. For comparison, a coulombic efficiency of 87% and a utilization ratio of 54% for the M10AB10 electrode are observed in the first cycle, which are lower than the corresponding values for the electrode composite that includes TiH_2 , indicating the positive function of electronic conduction pathway supplied by TiH_2 addition. The comparison results of electrode utilization and coulombic efficiency are depicted in Fig. 4-7(c). These results indicate that TiH_2 can be used instead of AB to improve the dynamic performance of the electrode reactions because of its high electronic conductivity. However, the capacity corresponding to TiH_2 decreased dramatically with increasing MgH_2 content; for the MT73AB10 electrode, no plateau assigned to TiH_2 was observed.

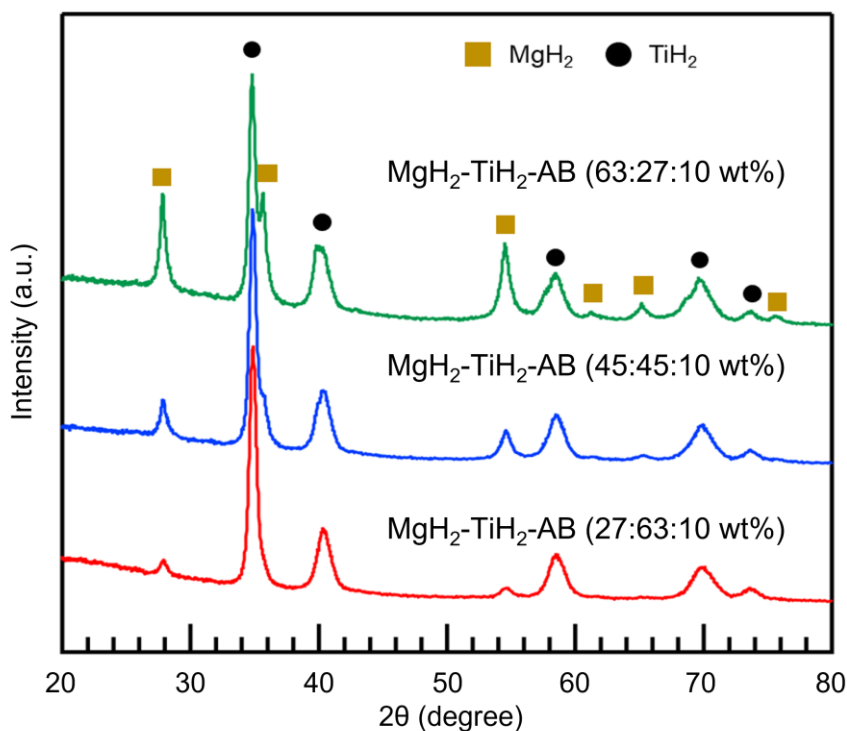


Figure 4-6. XRD profiles for various initial MgH_2 - TiH_2 -AB (27:63:10, 45:45:10, and 63:27:10 wt%, respectively) electrode composites.

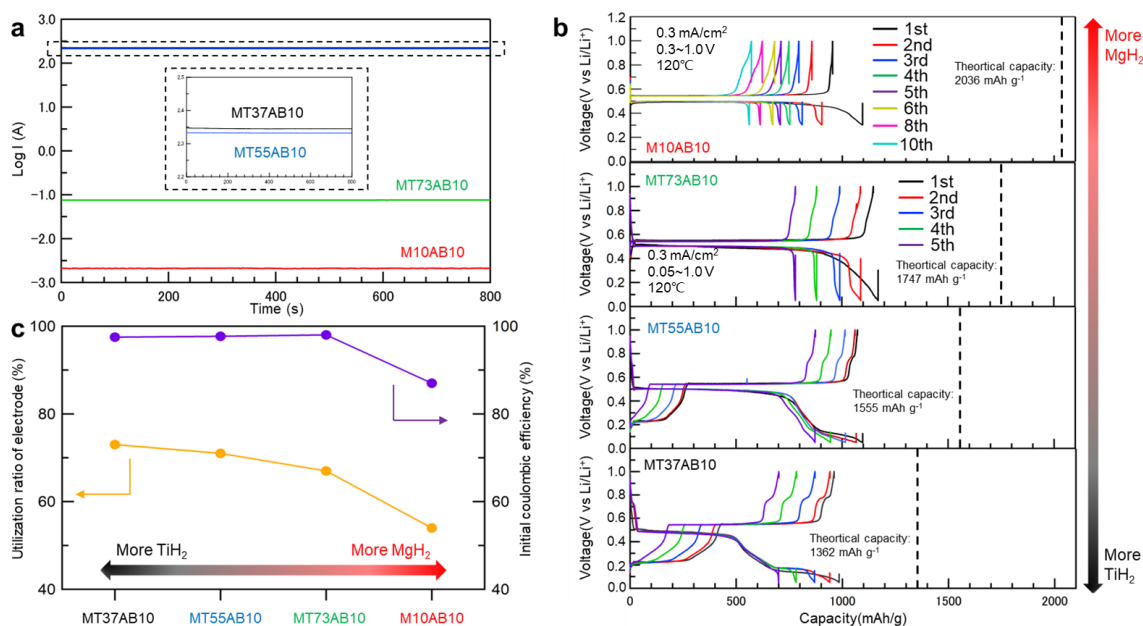


Figure 4-7. (a) Polarization current–time curves for electrodes under 0.1 V (the dotted-line square below represents the enlarged view of the upper square); (b) charge–discharge voltage profiles for $\text{MgH}_2\text{--TiH}_2\text{--AB}$ (27:63:10, 45:45:10, and 63:27:10 wt%) electrodes and $\text{MgH}_2\text{--AB}$ (90:10 wt%) electrodes. The dotted lines in the Fig. 3(b) represent the theoretical capacity of each electrode. (c) Comparison of utilization ratio and coulombic efficiency

Electrochemical measurements were conducted to investigate the cause of the decrease in capacity attributed to TiH_2 when the content of MgH_2 was increased. The $\text{MgH}_2\text{--TiH}_2\text{--AB}$ (49:21:30 wt%) electrode composite (which has the same $\text{MgH}_2\text{:TiH}_2$ ratio as that for MgTi73AB10) was used to evaluate the charge-discharge performance (Fig. 4-8). The plateau for TiH_2 was clearly observed with a high capacity (287 mAh/g, 956 mAh/g based on TiH_2 weight). The insufficient electron conductivity pathways and relatively large volume expansion, which the addition of AB can resolve, are considered the two main reasons for the low capacity of TiH_2 in the MgTi73AB10 electrode. With increasing content of MgH_2 , which reacted with Li before TiH_2 , the

amount of LiH formed as an electronic insulator in the electrode layer increased (hypothesis 1). The increased volume expansion might destroy the interface between TiH_2 and the electronic conductor (hypothesis 2). Both will inhibit the reaction of Li with TiH_2 . The two hypotheses are considered to explain the decrease in capacity assigned to TiH_2 with increasing MgH_2 content. In addition, the plateau corresponding to TiH_2 appeared and indicated a large capacity in the $\text{MgTi}_{73}\text{-AB}_{10}$ discharge-charge curves corresponding to a low current density of 0.05 mA cm^{-2} below 0.3 V (Fig. 4-9), indicating that the electrode reaction of TiH_2 (current density: 0.3 mA cm^{-2}) is mainly inhibited by insufficient electronic conductivity. Moreover, the capacity corresponding to the plateau at 0.8 V decreased with decreasing TiH_2 content in the electrode (Fig. 4-7(b)), indicating that this reaction is also limited by the diminished electronic conductivity. For the electrodes used 10 wt% AB and charge-discharged with 0.3 mA cm^{-2} , no capacity corresponding to the Li-Mg alloy reaction (0.15 V) was observed ^[13,16], which is speculatively attributed to the low AB content. These results indicate that, when the TiH_2 content is low, the TiH_2 electrode reaction kinetics are affected by the large amount of LiH formed via the MgH_2 electrode reaction, which subsequently causes the insufficient electronic conductivity and decreased capacity.

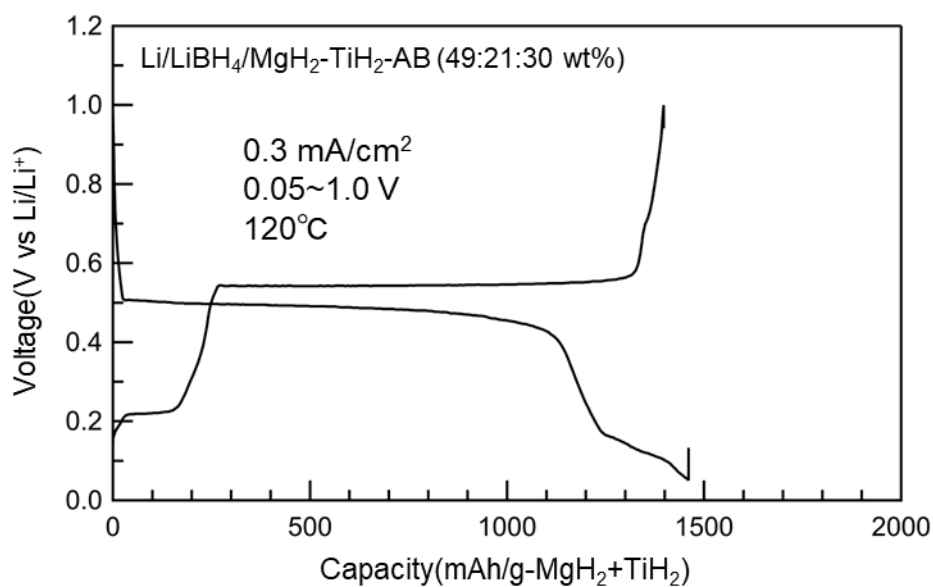


Figure 4-8. Charge-discharge voltage profiles for $\text{MgH}_2\text{-TiH}_2\text{-AB}$ (49:21:30 wt%) electrode composite.

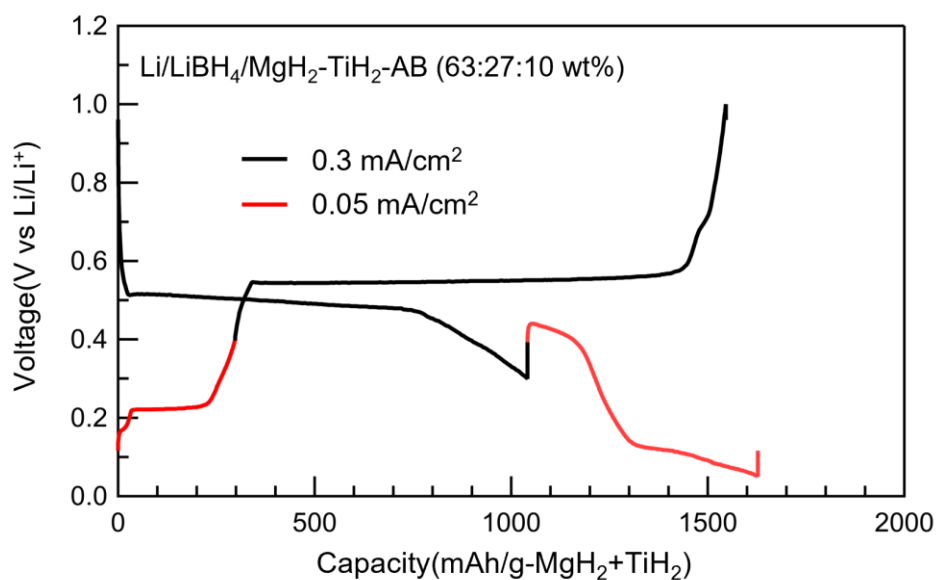


Figure 4-9. Charge-discharge voltage profiles for $\text{MgH}_2\text{-TiH}_2\text{-AB}$ (63:27:10 wt%) electrode composite with current density of 0.3 mA/cm^2 before 0.3 V and after 0.05 mA/cm^2 current density for discharging to 0.05 V .

To investigate the reaction mechanism for the $\text{TiH}_2\text{-MgH}_2\text{-AB}$ electrode with a low loading of AB, I carried out *ex situ* XRD measurements of $\text{MgTi}_{55}\text{-AB}_{10}$ in different states (Fig. 4-10). The right graphs are the enlarged view of the areas enclosed by dotted lines in the center graph. In the XRD patterns corresponding to the lithiation state at 0.3 V, the peaks due to MgH_2 at $2\theta=35.75^\circ$, 39.9° , and 54.64° in the pattern of the initial state disappeared and peaks associated with Metallic Mg and LiH appeared because of the lithiation of MgH_2 . The peaks corresponding to TiH_2 remained unchanged in the initial state, suggesting that the reaction of Li and TiH_2 did not occur at potentials greater than 0.3 V. After further lithiation to 0.05 V

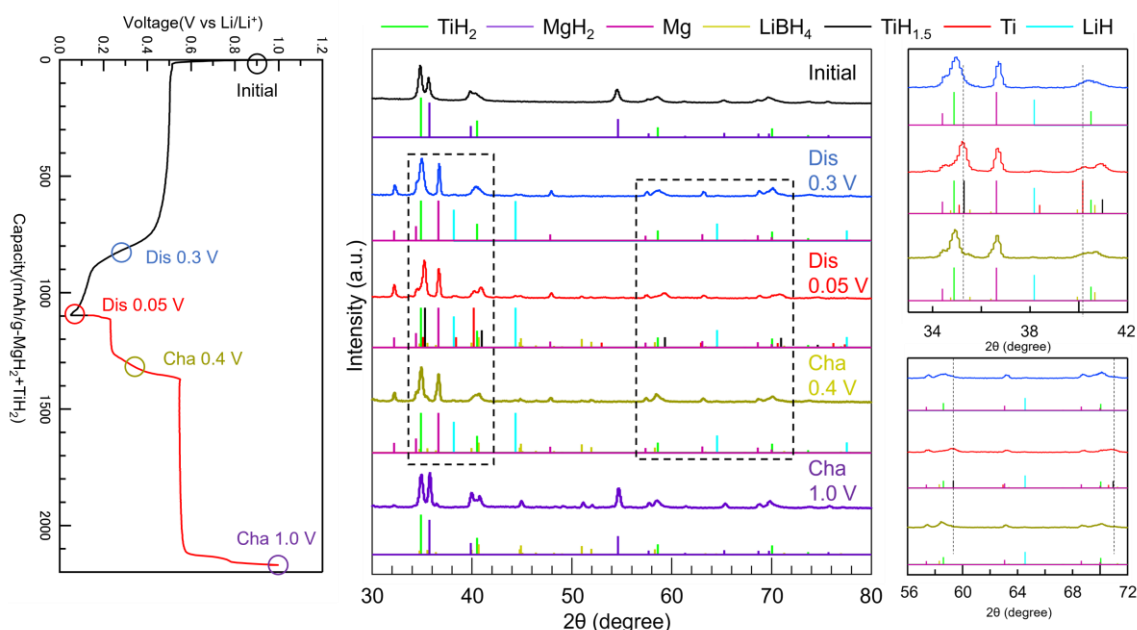
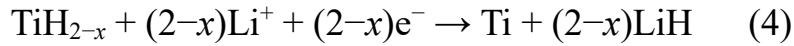
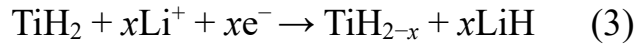


Figure 4-10. Comparison of *ex situ* XRD patterns for different states during initial charge–discharge cycles for $\text{MgH}_2\text{-TiH}_2\text{-AB}$ (45:45:10 wt%) composite electrode. The right graphs are the enlarged view of the areas enclosed by dotted lines in the center graph. Patterns generated from structures of possible products within the ICSD are shown for reference. (TiH_2 ICSD: 638505, MgH_2 ICSD: 155807, Mg ICSD: 77908, $\text{TiH}_{1.5}$ ICSD: 63427, Ti ICSD: 76265, LiH ICSD: 61751)

(Dis 0.05 V), regarding the slope between 0.3 and 0.15 V and the plateau at 0.15 V, the 111 peak of the TiH_2 at 35.8° shifted to a higher diffraction angle and the $\text{TiH}_{1.5}$ phase ($2\theta=35.8^\circ, 41^\circ, 59^\circ, 70.5^\circ$) was detected. Moreover, the 111 peaks corresponding to the Ti phase peak at 39° also appeared with a low intensity. This result is ascribed to the insertion of Li^+ ions into the $\text{TiH}_{1.5}$ phase to form a Ti phase. Therefore, the slope and plateau are considered to correspond to the following reactions:



Notably, the capacity attributed to TiH_2 is 600 mAh/g, indicating that ~40% of the active material was unreacted, which might be attributable to the low content of AB. Similar to the results for MgTi55-AB10, diffraction peaks due to Mg-Li alloy are also not observed in the pattern corresponding to the Dis 0.05 V state, suggesting that Li-Mg alloy formation might be limited by the addition of TiH_2 and low content of AB. When the cell was charged to 0.4 V, the peaks assigned to the TiH_2 phase appeared again (accompanied by a decrease in intensity of the $\text{TiH}_{1.5}$ and Ti phases) after Li extraction, indicating the transformation from $\text{TiH}_{1.5}$ and Ti to the TiH_2 phase, corresponding to the plateau at ~1.5 V in the charging curve. With further charging (Cha 1.0 V), the diffraction peaks for MgH_2 reappeared and those for Metallic Mg phases disappeared. These results are attributed to the

reaction of Mg and LiH, which corresponds to ~ 0.5 V in the charging curve. The XRD pattern after the charging process is similar to that for the initial state, which shows only peaks associated with MgH_2 and TiH_2 , suggesting that the MgH_2 - TiH_2 electrode is highly reversible even when the AB content is low.

To discuss the difference in the reaction mechanism between different electrodes, I collected XRD patterns corresponding to the lithiated state (0.05 V) (Fig. 4-11). Obviously, in the patterns for MgTi37-AB10 and MgTi55-AB10 , the TiH_2 peaks entirely disappeared and the peaks assigned to TiH_{2-x} remained with high intensity, indicating that the Ti metal formation process

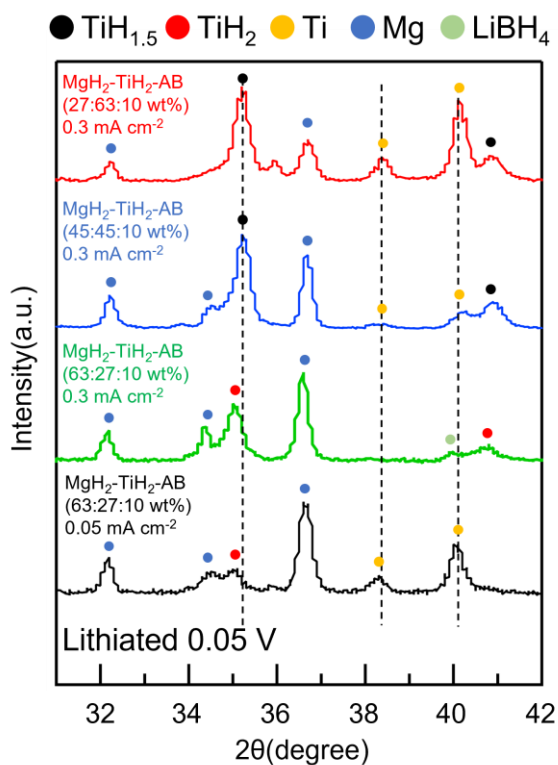
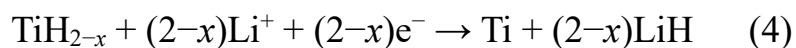


Figure 4-11. Comparison of *ex situ* XRD patterns for 0.05 V lithiated state during initial lithiation process of different MgH_2 - TiH_2 -AB composite electrodes.

was mainly limited. These results are tentatively attributed to the LiH, which is formed by the reaction of MgH₂ and TiH₂, located near the TiH_{2-x} inhibiting the contact with electrons and thus limiting the reaction between TiH_{2-x} and Li to form Ti metal. Compared with the pattern for MgTi55-AB10, that for MgTi37-AB10 shows a higher Ti metal peak intensity because the MgH₂ content of MgTi55-AB10 is greater than that of MgTi37-AB10 (a larger amount of LiH is formed). For the MgTi73-AB10, TiH₂ peaks remain with a relatively high intensity and no peaks due to TiH_{2-x} are observed, suggesting that almost no reaction occurred between Li and TiH₂, consistent with the results of the charge-discharge measurements. However, in the XRD pattern for MgTi73-AB10 (low current density), the Ti metal peak intensity increased significantly and no peak for TiH_{2-x} was observed; the pattern also shows that a small amount of TiH₂ remained. These results indicate that the reaction,



which is inhibited by an insufficient electron pathway (caused by the LiH electronic insulator), can be entirely promoted by a low current density. The remaining unreacted TiH₂ is considered to be a result of the volume expansion of MgH₂ (which destroys the interface with the TiH₂ active material) and/or isolation from the electron conduction paths. When these results are considered in combination with those previously discussed, the

loss capacity for TiH_2 is mainly caused by the equation 4, even though the equation 3 is completed. Therefore, the LiH formed via the reaction equation 4 will also inhibit the subsequent reaction of TiH_2 .

To investigate the effect of reacted MgH_2 on the reaction kinetics of TiH_2 , I investigated the evolution of the electrical resistance with the lithiation process for the MgTi-AB10 and Ti-AB (90:10 wt%) electrodes using EIS measurement (Fig. 4-12). The impedance profiles for the initial state of the different electrodes include a straight line corresponding to the Warburg resistance (semi-infinite diffusion of the planar electrode), indicating low resistance in the charge transfer process because of the high operating temperature ^[17]. During lithiation process, the decrease in the slope of the straight line may be attributed to uneven and rough electrode surface caused by electrode reactions. For the electrodes composed of MgH_2 and TiH_2 , as the lithiation process proceeds to 0.3 V (TiH_2 reaction occurs), a semicircle appears in the higher-frequency region (0.1 MHz to 0.261 Hz). This is attributed to the increased charge transfer resistance (calculated by the equivalent circuit method; the values are shown in Table 4-2, and the equivalent circuit and fitting result are shown in Fig. 4-13(a)). The increase in the charge transfer resistance (observed in Fig. 4-12(b,c)) was caused by the formation of the LiH insulator (which will inhibit the occurrence of electrode reaction of TiH_2 active material). As shown in the Fig. 4-12(b,c)

and Table 4-2, the charge transfer resistance decreased with decreasing content of MgH_2 in the electrode, due to less generation of LiH . For the 0.05 V lithiated states, because of the further lithiation of MgH_2 and TiH_2 , an increase in the charge transfer resistance was observed when an electrode containing MgH_2 was used. The illustration of reaction mechanism was shown in Fig. 4-12(d). In addition, because of the sufficient electron conduction pathways provided by TiH_2 and AB, a semicircle was not observed for the TiH_2 -AB (90:10 wt%) electrode in either the 0.3 or 0.05 V lithiated state, indicating a low charge transfer resistance. The combination of the EIS measurement results for the TiH_2 -AB (90:10 wt%) electrode and the $\text{Li}/\text{LiBH}_4/\text{Li}$ symmetrical cell (Fig. 4-13(b)) suggests that the interfacial resistance between Li and the LiBH_4 electrolyte has little effect on the charge transfer resistance. These results indicate that the high content of MgH_2 , which leads to an increase in LiH production, dramatically limits the reaction kinetics of TiH_2 . The electrons cannot easily contact the TiH_2 active material because of the inhibition resulting from the *in situ* formation of the LiH insulator, thus resulting in a low electrode utilization at a high current density.

To further investigate the influence of ionic and electron conduction pathways on utilization ratio of active materials. The volume ratio of ionic and electron conduction pathways within the anode and comparison between MgH_2 and TiH_2 capacity are shown in Fig. 4-14. Volume ratios were

calculated by the follow formulas:

Volume ratio of LiH/anode (ion conduction path):

$$\text{LiH}(\text{volume})/(\text{LiH}+\text{MgH}_2+\text{Mg}+\text{Ti}+\text{TiH}_2+\text{AB})(\text{volume})$$

Volume ratio of TiH₂+AB/anode (electron conduction path)

$$(\text{TiH}_2+\text{AB})(\text{volume})/(\text{LiH}+\text{MgH}_2+\text{Mg}+\text{Ti}+\text{TiH}_2+\text{AB})(\text{volume})$$

Initial volume ratio of TiH₂+AB/anode (electron conduction path)

$$(\text{TiH}_2+\text{AB})(\text{volume})/(\text{MgH}_2+\text{TiH}_2+\text{AB})(\text{volume})$$

From Fig. 4-14(a), as the amount of TiH₂ addition increases, the volume ratio of TiH₂+AB/anode rises, indicating that the electronic conduction pathways are further optimized. Consequently, the initial capacity of MgH₂ also improves with the increase in electronic conduction pathways (see Fig. 4-14(b)). During the lithiation process, when the voltage drops to 0.3 V (at which TiH₂ begins to undergo an electrode reaction), Fig. 4-14(a) shows that although the electrode reaction of MgH₂ produces LiH, resulting in an increased volume ratio of LiH, this change may facilitate the formation of lithium-ion conduction channels. However, Fig. 4-14(b) reveals that the capacity of TiH₂ decreases as the increase of ion conduction pathways.

On the other hand, due to the volume expansion of MgH₂ after the reaction, the overall volume ratio of TiH₂+AB/anode decreases at 0.3 V. With the further increase in MgH₂ addition, the volume ratio of TiH₂+AB/anode continues to decrease, indicating a reduction in electronic conduction

pathways. This trend is consistent with the change in TiH_2 capacity (Fig. 4-14(b)). Therefore, in cases with a low amount of conductive additives, the reduction in electronic conduction pathways has a more significant impact on the utilization of active materials.

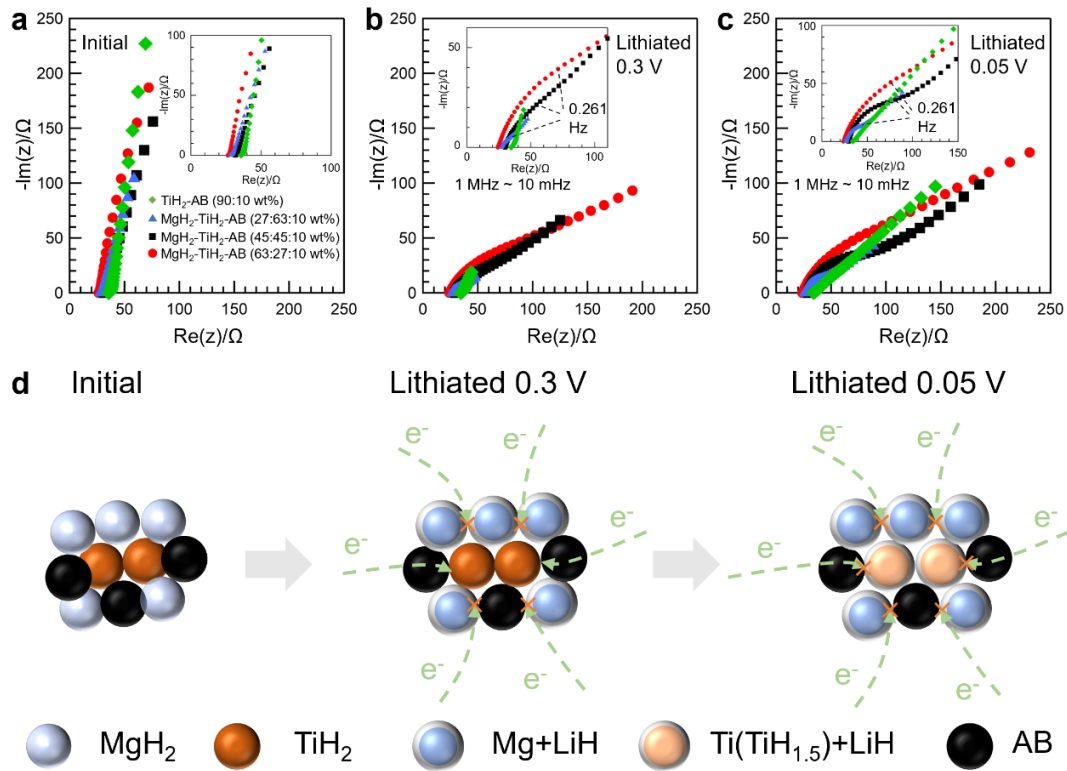


Figure 4-12. EIS plots for TiH_2 -AB electrode (90:10 wt%) and MgH_2 - TiH_2 -AB electrodes (27:63:10 wt%, 45:45:10 wt% and 63:27:10 wt%, respectively): (a) initial state, (b) lithiated 0.3 V state, and (c) lithiated 0.05 V state. (d) Illustration of reaction mechanism.

Table 4-2. Charge transfer resistance values for different electrode composites.

Electrode composite	Charge transfer resistance (0.3 V-counter electrode)	Charge transfer resistance (0.05 V-counter electrode)	Charge transfer resistance (0.3 V-working electrode)	Charge transfer resistance (0.05 V-working electrode)
MgH_2 - TiH_2 -AB (63:27:10 wt%)	2.5 Ω	2.6 Ω	158.7 Ω	204.7 Ω
MgH_2 - TiH_2 -AB (45:45:10 wt%)	1.0 Ω	2.3 Ω	91.42 Ω	109.5 Ω
MgH_2 - TiH_2 -AB (27:63:10 wt%)	0.4 Ω	2.0 Ω	21.51 Ω	57.48 Ω

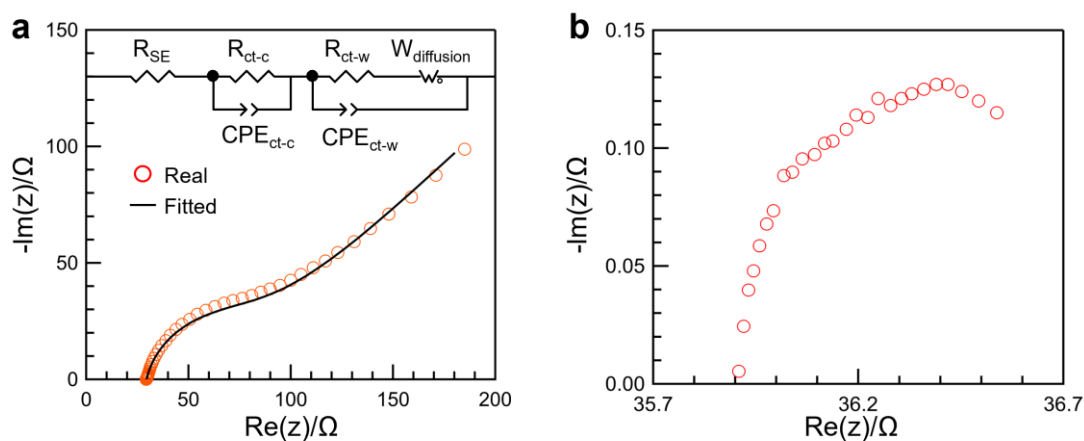


Figure 4-13. (a) Equivalent circuit model and fitting results for $\text{MgH}_2\text{-TiH}_2\text{-AB}$ (45:45:10 wt%) electrode at 0.05 V and (b) EIS plot for $\text{Li/LiBH}_4/\text{Li}$ symmetrical cell.

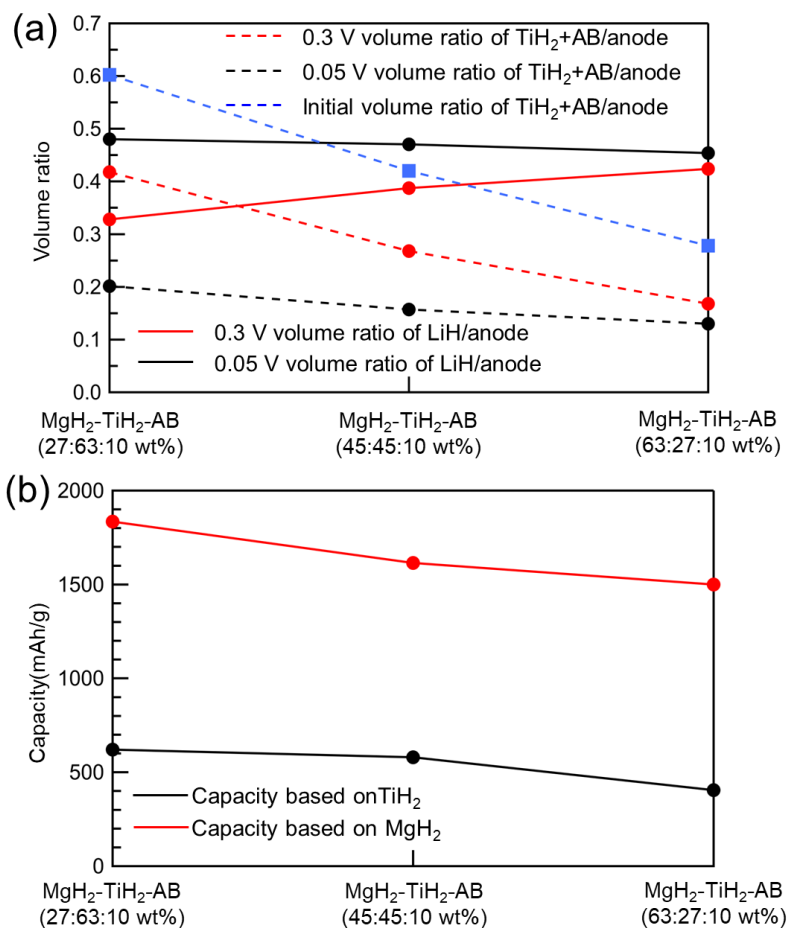


Figure 4-14. (a) Volume ratios of $\text{TiH}_2\text{+AB/anode}$ and LiH/anode in different charge-discharge states. (b) Comparison of capacity based on TiH_2 and MgH_2 .

4.3.3. Comparison between $\text{MgH}_2\text{-TiH}_2\text{-AB}$ and $\text{MgH}_2\text{-TiH}_2\text{-VCGF}$ composite anodes

As previously mentioned, the loss of a continuous electron pathway is considered an important reason for the poor battery performance of $\text{MgH}_2\text{-TiH}_2$ electrodes. Therefore, to improve the charge-discharge performance of the ASSB-based $\text{MgH}_2\text{-TiH}_2$ electrode composite, it is important to create sufficient electron conduction paths in the electrode layer. VGCF can be used to enhance the cycling performance because it is more dispersible than AB during the ball-milling process,^[5,18] thus enabling a uniform distribution and the formation of an intimate interface with the active materials. The charge-discharge performance of the $\text{MgH}_2\text{-TiH}_2\text{-VGCF}$ (45:45:10 wt%) (MgTi55-VG10) electrode is shown in Fig. 4-15(a, b). Notably, the initial discharge capacity is improved from 1097 mAh/g (MgTi55-AB10) to 1342 mAh/g with increasing electrode utilization ratio. The increase in capacity is mainly caused by the enhanced capacity corresponding to TiH_2 , indicating that the equation 4 is promoted by the addition of VGCF. Meanwhile, the MgTi55-VG10 electrode exhibited improved cycling performance, where, after 10 cycles, the obtained discharge capacity was 1103 mAh/g (capacity retention: 82.2%). In the charge curve, in addition to the plateau associated with the regeneration of TiH_2 and MgH_2 , a short plateau appeared at 0.16 V (no observation in the Fig. 4-7(b)), which is attributed to Li extraction from Li-

Mg alloy,^[13] suggesting the occurrence of a Li-Mg alloy reaction during the lithiation process. These results suggest the electrode reactions (TiH_2 , Mg-Li alloy, and MgH_2) are promoted by the sufficient electron conduction pathways supplied by the added VGCF. The exact mechanism, however,

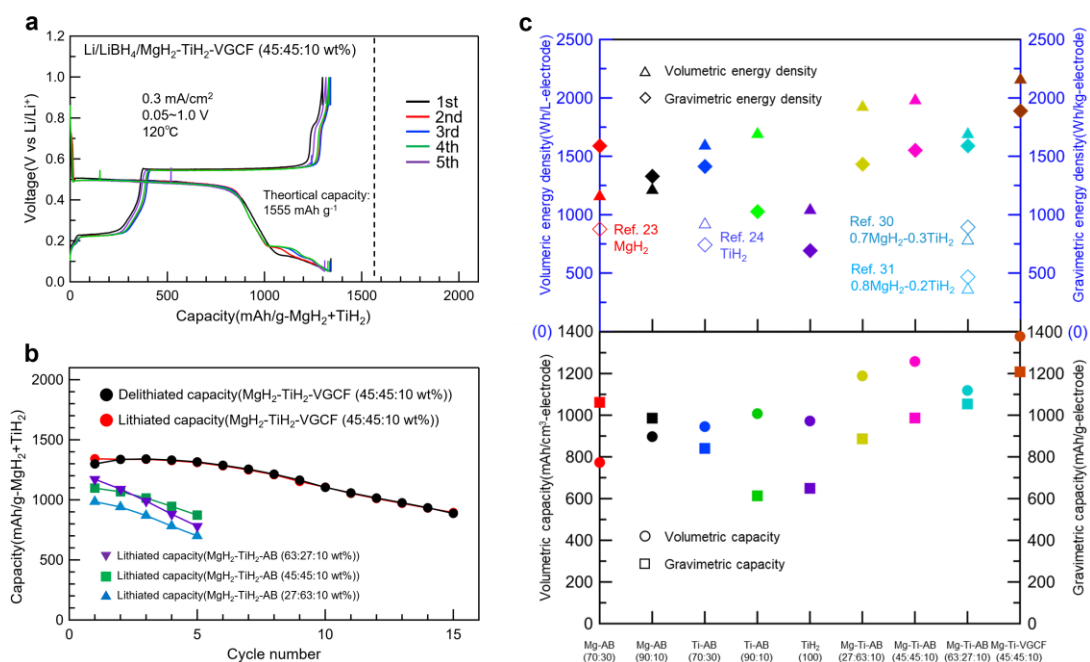


Figure 4-15. (a) Charge–discharge voltage profiles for $\text{MgH}_2\text{-TiH}_2\text{-VGCF}$ (45:45:10 wt%) composite electrode and (b) equivalent cycling performance of same cell over 15 cycles. (c) Comparison of initial lithiated volumetric/gravimetric capacity and initial reversible volumetric/gravimetric energy density of as-prepared electrodes in this work and a previously reported metal hydride anode (based on the weight and volume of the anode). (A full-cell discharge curve was assumed from the delithiation curve of the half-cell, and the energy density was calculated by integrating it. Li_2S (redox potential: 2.1 V vs. Li/Li^+) was used as cathode material for the full-cell.)

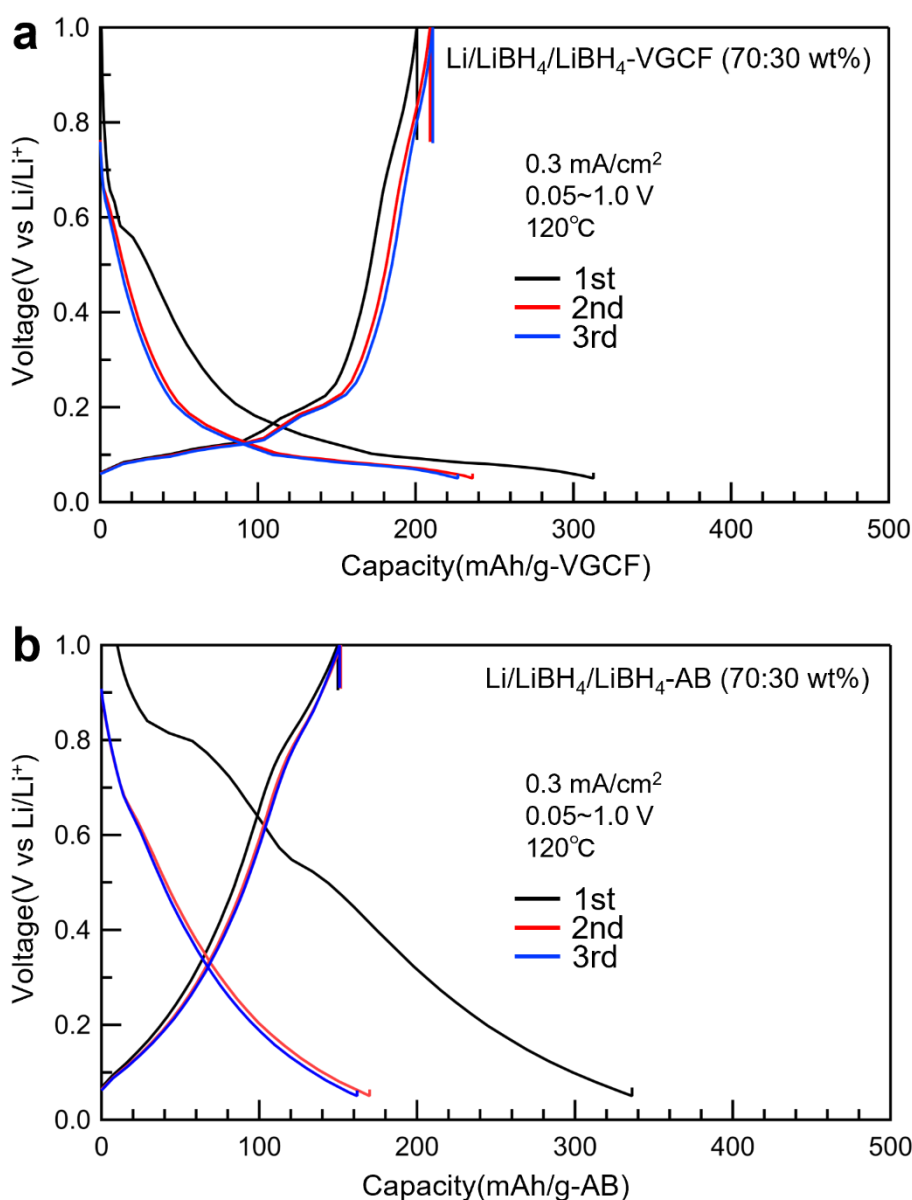


Figure 4-16. Charge-discharge voltage profiles for (a) the LiBH₄-VGCF (70:30 wt%) electrode composite and (b) LiBH₄-AB (70:30 wt%) electrode composite against Li.

requires further discussion. Given that VGCF also can store Li⁺ ions, to investigate the contribution of VGCF to the total capacity, I constructed a Li/LiBH₄/LiBH₄+VGCF (70:30 wt%) all-solid-state cell and measured its battery performance. From the results of the charge-discharge measurements (Fig. 4-16), a slope from 0.4 to 0.05 V is observed and an initial discharge

capacity of 315 mAh/g is indicated. By conversion to total capacity, Li^+ insertion into VGCF is estimated to contribute 30 mAh/g to the capacity (1342 mAh/g) of the MgTi55-AB10 electrode, indicating that the capacity under 0.3 V is mainly associated with the reaction of Li with TiH_2 . For comparison, the charge-discharge performance of an Li/LiBH₄/LiBH₄+AB (70:30 wt%) all-solid-state cell was also measured and an initial lithiation capacity of 336 mAh/g was observed (Fig. 4-15(b)). When VGCF was used as a carbon additive, the electrochemical performance was substantially enhanced because of the formation of sufficient electron pathways.

The actual initial discharge capacity of different electrode composites depending on volume and weight were calculated; the results are shown in the lower part of Fig. 4-15(c), and details are provided in Table 4-3. The left axis, which is related to the volumetric capacity, shows that the electrode based on MgH₂-AB (70:30 wt%) exhibited the lowest value of 773 mAh/cm³ because of its low MgH₂ density and high AB content. When the MgH₂ content was increased from 70 to 90 wt%, the volumetric capacity increased from 778 to 898 mAh/cm³ because the low AB content increased the density of the electrode composite even though the gravimetric capacity decreased. When TiH_2 was used as the active material, the volumetric capacity increased further because of its high density. In addition, when the electrode based on the MgH₂- TiH_2 active material was used, because of the combination of the

high electron conductivity/density of TiH_2 and the high theoretical capacity of MgH_2 , both the volumetric and gravimetric capacities improved. With increasing content of MgH_2 , MgTi73-AB10 showed a decrease in volumetric capacity because of the high MgH_2 content (low density). Importantly, when VGCF was used as the carbon additive to promote the electrode reaction, the MgTi55-VG10 achieved a volumetric capacity of 1378 mAh/cm^3 , which is almost twice that for $\text{MgH}_2\text{-AB}$ (70:30%). However, with respect to gravimetric capacity, MgTi55-VG10 also showed the highest capacity of 1208 mAh/g . To characterize the difference in the energy density for the various anodes (excluding the effects from the weight and volume of the cathode), Li_2S , which has been previously incorporated into a full cell with a metal hydride anode [31], was assumed as a cathode material with a redox potential of 2.1 V vs. Li^+/Li . The energy density based on the anode can be calculated as

Table 4-3. Properties of prepared electrode composites.

Electrode composite	Theoretical capacity mAh/g	Specific capacity mAh/g	Volumetric capacity (mAh/cm ³)	Gravimetric capacity (mAh/g)	Areal capacity (mAh/cm ²)	Volumetric energy density (Wh/L)	Gravimetric energy density (Wh/kg)	Active material loading (mg cm ⁻²)	Electrode thickness (μm)
$\text{MgH}_2\text{-AB}$ (70:30 wt%)	2036	1517	773	1062	8.1	1157	1589	5.35	105
$\text{MgH}_2\text{-AB}$ (90:10 wt%)	2036	1096	898	986	7.5	1209	1329	6.88	84
$\text{TiH}_2\text{-AB}$ (70:30 wt%)	1074	1201	945	841	6.4	1589	1414	5.35	68
$\text{TiH}_2\text{-AB}$ (90:10 wt%)	1074	681	1008	613	4.7	1689	1028	6.88	47
TiH_2 (100 wt%)	1074	649	973	649	5.0	1037	692	7.64	51
$\text{MgH}_2\text{-TiH}_2\text{-AB}$ (27:63:10 wt%)	1362	985	1189	887	6.8	1921	1433	6.88	57
$\text{MgH}_2\text{-TiH}_2\text{-AB}$ (45:45:10 wt%)	1555	1097	1258	987	7.5	1977	1552	6.88	60
$\text{MgH}_2\text{-TiH}_2\text{-AB}$ (63:27:10 wt%)	1747	1171	1119	1054	8.1	1687	1589	6.88	72
$\text{MgH}_2\text{-TiH}_2\text{-VGCF}$ (45:45:10 wt%)	1555	1342	1378	1208	9.2	2154	1888	6.88	67

$$\text{Energy density (Wh/kg)} = \int_0^{C_{\text{rev}}} V dC_{\text{anode}} \quad (5)$$

$$\text{Energy density (Wh/L)} = \frac{m}{v} \int_0^{C_{\text{rev}}} V dC_{\text{anode}} \quad (6)$$

where V is the voltage of the battery, C_{anode} is the capacity based on anode weight, C_{rev} is the value of the initial reversible capacity, and m and v are the mass and volume of the anode, respectively. The calculation results are shown in the upper part of Fig. 4-15(c). The higher improvement in the energy density (depend on the anode) was thus found (volumetric capacity ratio of MgTi55-VG10/Mg-AB73: 1.782, volumetric energy density ratio of MgTi55-VG10/Mg-AB73: 1.864) because of the low reaction potential of TiH_2 . The energy density of previously reported metal hydride anodes was also calculated using the same method, and the values were found to be relatively lower. I speculate that the addition of TiH_2 to electrode composites not only increases the volumetric energy density but also the gravimetric energy density, both of which are desirable for developing high-energy-density ASSB systems. However, the capacity decayed dramatically even using VGCF as carbon additive, enhancement of cycling performance is necessary.

4.4 Conclusion

TiH₂ was used as an active material that forms a solid electrolyte *in situ* in an ASSB. The resultant ASSB showed a large capacity of 1201 mAh/g and a reversible capacity of 1145 mAh/g despite no solid electrolyte being added to the electrode composite. The TiH₂ active material was also more suitable as an anode for high-voltage batteries because of its low redox potential of 0.2 V. In addition, because of the high electronic conductivity of TiH₂, TiH₂-AB (90:10 wt%) electrode and TiH₂ (100 wt%) electrode exhibited a high initial lithiation capacity of 681 and 649 mAh/g, respectively. Compared with previously reported metal-hydride anodes, our MgH₂-TiH₂-AB electrode achieved a higher energy density, even when the AB content of the electrode was 10 wt%, indicating the feasibility of using TiH₂ as the conductor additive. Moreover, when VGCF was substituted for AB as the carbon additive, remarkable improvements in the charge-discharge performance (initial lithiation capacity: 1342 mAh/g (electrode utilization ratio: 86%)) and energy density (increase in volumetric energy density from 1977 Wh/L (AB) to 2153 Wh/L (VGCF)) were attained as a result of continuous electron pathways provided by the VGCF; the detailed mechanisms will be evaluated in a future study. The results showed that the TiH₂ bifunctional material (that functions as both an active material that

forms a solid electrolyte *in situ* and a conductor additive) not only enables smaller amounts of solid electrolytes and carbon additives to be used in the electrode composites but also exhibits a high capacity and low potential. I believe this material will play a critical role in the development of high-energy-density negative electrode materials with a high active material content for practical use in ASSBs.

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Chapter 5

Spontaneous Densification of Electrode by Chemical Reaction to Stabilize Metal Hydride Anode with High Active Material Content

5.1 Introduction

Metal hydrides such as MgH_2 exhibit high theoretical capacities and low electrochemical potentials and thus have been considered as potential anode materials for use in high-energy-density ASSBs.^[1–4] Metal hydride anodes also exhibit lower polarization than other types of conversion anodes because H^- migration occurs more readily during the reversible lithiation and delithiation of MgH_2 .^[5] For this reason, MgH_2 is often combined with LiBH_4 to produce the solid electrolyte for ASSBs. LiBH_4 is employed because this compound tends to show high Li ion conductivity (phase transition at 115 °C)^[6,7] and simultaneously facilitates H^- transport via the hydrogen exchange effect.^[3,8] These factors promote MgH_2 electrode reactions and so improve electrochemical performance. Hence, improving the electrochemical activity of MgH_2 by promoting the transport of H^- within the electrode is an effective

approach to increasing battery performance and so has been studied in detail. As an example, electrodes based on Nb₂O₅-doped MgH₂ and MgH₂-TiF₃ composites have been reported to deliver excellent charge-discharge performance.^[9,10] This is attributed to the ability of both Nb₂O₅ and TiF₃ to promote hydrogen reactions on MgH₂. These compounds have also been shown to act as catalysts to enhance hydrogen absorption/release kinetics and/or reduce the hydrogen absorption/release temperature for MgH₂.^[11,12] TiH₂ in particular has been intensively researched as a dynamic additive intended to improve the de/rehydrogenation characteristics of MgH₂.^[13–15] On this basis, the electrochemical properties of MgH₂ appear to be improved by the addition of TiH₂.

As described in Chapter 4, due to the high electrical conductivity (10⁴ S/cm) of TiH₂,^[16] the carbon additive content of the electrode can be decreased. A MgH₂-TiH₂-AB (AB = acetylene black) electrode having a 45:45:10 wt% composition exhibited a high specific capacity of 1097 mAh/g even with a minimal proportion (10 wt%) of conducting agent.^[17] However, the electrochemical activities of MgH₂ and TiH₂ can be reduced as a consequence of the significant interfacial resistance resulting from poor solid-solid contact,^[17] which may restrict the ability of TiH₂ to promote the electrode reaction of MgH₂. Moreover, both MgH₂ and TiH₂ exhibit large volume changes during the lithiation and delithiation processes that can lead

to the pulverization of active materials. This phenomenon can be aggravated during repeated cycling, resulting in rapid deterioration of the reversible specific capacity of the battery.

Compared with traditional solid-solid interfaces formed by pressing or mechanical milling processes, the interfaces generated by chemical reactions between solid compounds are typically more intimate and stable because of surface mass transportation effects.^[18] Based on previous work, the MgH_2/Mg and TiH_2/Ti reaction potentials are $E_{\text{MgH}_2} = 0.5 \text{ V vs Li}^+/\text{Li}$ and $E_{\text{TiH}_2} = 0.15 \text{ V vs Li}^+/\text{Li}$, respectively.^[1,19,20] These values can be evaluated based on the equation

$$\Delta G = -nF(E_1 - E_2) \quad (1)$$

where ΔG is the Gibbs free energy change, n is the moles of electrons involved in the reaction, F is Faraday's constant, and E_1 and E_2 are the redox potentials for the reduced and oxidized reactant, respectively. In the case that the values of E_{MgH_2} and E_{TiH_2} are substituted for E_1 and E_2 , respectively, a negative ΔG value is obtained, indicating that the reaction $\text{MgH}_2 + \text{Ti} \rightarrow \text{Mg} + \text{TiH}_2$ will proceed spontaneously. On this basis, it appears that an intimate interface between MgH_2 (regenerated during the delithiation process) and TiH_2 can be produced *in situ* via the reaction between MgH_2 and Ti . From the previous study, Mg and TiH_{2-x} can form by ball-milling a MgH_2+Ti composite for 15 h,^[21] which is consistent with our

above inference that MgH_2 can react with Ti. However, the mechanism of this reaction has not been thoroughly explained and applied to enhance electrode performance.

In previous research, the construction of so-called plum pudding hybrids, where the former comprise particles of active materials and the latter comprises a continuous matrix, was found to mitigate changes in volume associated with lithiation and delithiation.^[22] Specifically, in the case that the continuous matrix is rigid, this matrix can supply compressive stress to mechanically restrict the volume expansion of the active materials during lithiation and so reduce the maximum stress experienced by particles of these materials.^[22,23] The more rigid morphology resulting from the reaction between MgH_2 and Ti can provide this physical support to suppress the volume change and thus improve the cycling stability of the electrode.

The present study examined the electrode composites MgH_2 - TiH_2 -AB (27:63:10 wt%) (sample 1) and MgH_2 -Ti-LiH-AB (27:47:16:10 wt% with a MgH_2 :Ti:LiH molar ratio of 1:1:2) (sample 4). Sample 1 was assessed for comparison purposes (to maintain consistency with sample 4, the MgH_2 and AB contents were also set to 27 wt% and 10 wt%, respectively, and the remaining 63 wt% was allocated to TiH_2) and to clarify the effect of TiH_2 addition on the reaction kinetics of MgH_2 . Sample 4 was investigated with regard to its charge-discharge properties to ascertain any improvements in

electrochemical performance stemming from the *in situ* formation of a solid interface due to the reaction between MgH_2 and Ti. The TiH_2 produced by this reaction was also expected to supply electronic conduction pathways similar to those provided by TiH_2 originally mixed into the electrode composite. Both of MgH_2 and TiH_2 can *in situ* form LiH to supply Li-ion conduction pathways and the content of solid electrolyte in the electrode can be decreased to 0 wt%.^[17,24] Therefore, the proportion of conductive agent in sample **4** was decreased to 10 wt% to allow more active material to be included and LiH was incorporated to react with Mg. To maintain the high conductivity of LiBH_4 , the battery operating temperature was set to 120°C. The reaction mechanisms associated with the MgH_2 and Ti in this mixture were examined by acquiring X-ray diffraction (XRD) data and using electrochemical characterization methods. Scanning electron microscopy (SEM) images were obtained from specimens in various charge-discharge states to investigate changes in morphology as MgH_2 -Ti-based electrodes were used. An electrode containing 90 wt% active material was fabricated and delivered exceptional electrochemical performance with a high reversible capacity of 830 mAh/g after 200 cycles and a current density of 1.0 mA/cm².

5.2 Experimental Section

5.2.1. Materials synthesis

The MgH_2 - TiH_2 -AB electrode composite (sample 1) without a solid electrolyte was prepared from commercial MgH_2 (95%, Fujifilm Wako), TiH_2 powder (95%, Sigma-Aldrich) and AB (97%, Denka) combined in a mass ratio of 27:63:10 followed by ball milling under an Ar atmosphere. In this process, the MgH_2 and TiH_2 serving as active materials were loaded into an 80 ml ZrO_2 milling jar together with AB in a 27:63:10 mass ratio (giving a total amount of 500 mg) along with 20 g of ZrO_2 balls each having a diameter of 3 mm. The mixture was subsequently milled for 30 min at a rate of 400 rpm. For comparison purposes, an electrode composite without a solid electrolyte was prepared by combining MgH_2 and AB at a mass ratio of 70:30. The same milling conditions used for the MgH_2 - TiH_2 -AB electrode composite were also used for this MgH_2 -AB, referred to herein as sample 2. To investigate the effects of Ti addition and the reaction between MgH_2 and Ti on electrochemical performance, MgH_2 - TiH_2 -Ti-LiH-AB (27:27:27:9:10 wt%) (sample 3) and MgH_2 -Ti-LiH-AB (27:47:16:10 wt%) (sample 4) were also prepared using the same milling conditions previously described. LiH was used to react any Mg produced as a consequence of the reaction between MgH_2 and Ti during delithiation. Specimens comprising Ti-LiH-AB

(67.5:22.5:10 wt%) (sample **5**), MgH_2 -LiH-AB (67.5:22.5:10 wt%) (sample **6**) and MgH_2 -Ti-AB (27:63:10 wt%) (sample **7**) were also fabricated to provide a better understanding of the role of each compound and to investigate the reaction mechanism.

5.2.2. Half-cell assemblies

Metallic Li/ LiBH_4 /electrode batteries were assembled by first manually pressing a Li foil disk onto a stainless-steel plate (SUS), adding 60 mg of LiBH_4 as the electrolyte and compacting the mixture at 255 MPa. A 6 mg quantity of the electrode composite was placed over top of the electrolyte layer followed by pressing at 318 MPa to complete the half-cell. A SUS plate with a diameter of 10 mm was used as the current collector. To limit the occurrence of Li dendrites, a Li-In alloy having a Li:In mass ratio of 1:21 was used as the counter electrode (potential compared to pure Li is 0.6 V). The same procedures were utilized to fabricate Li-In/ LiBH_4 /sample **1** and Li-In/ LiBH_4 /sample **4** half-cells.

5.2.3. Electrochemical Measurements

The half-cells were characterized by acquiring galvanostatic charge-discharge and galvanostatic intermittent titration technique (GITT) data at 120 °C, which was above the phase-transition temperature of LiBH_4 . During

each trial, a load of 2.16 C (0.6 mAh) was applied during the charge-discharge process at 0.5 mA/cm² with a relaxation time of 5 h using a battery tester (Hokuto Denko, HJ1020mSD8). The charge-discharge activities of MgH₂ and TiH₂ were separately evaluated by setting the voltage ranges to 0.3-1.0 V and 0.05-1.0 V, respectively. The standard rest time prior to acquiring charge-discharge data was 4 h. Additionally, 15 h and 60 h of prior rest time were used to investigate the relationship between rest time and reaction extent of MgH₂ and Ti. When using the Li-In alloy, the voltage range was set to -0.56 to 0.39 V. Electrochemical impedance spectroscopy (EIS) analyses were performed using an electrochemical workstation (Biologic, VSP) over the frequency range from 100 mHz to 1 MHz at an amplitude of 10 mV.

5.2.3. Characterization

Ex situ XRD patterns (Rigaku RINT-TTRIII) were obtained at different times during the charge-discharge process to elucidate the reaction mechanism associated with the MgH₂-Ti electrode composite. In addition, SEM (JSM-IT700HR, accelerating voltage of 10 kV) was used to investigate morphological changes associated with cycling. Ball-milled powder was used as SEM samples of initial state. Electrode layers (LiBH₄ (solid electrolyte layer) were detached from electrode layer as much as possible)

separated from the charge-discharged cells were used as SEM samples after charge-discharge measurement. The samples were transported to the SEM equipment in an Ar-filled sealed container to minimize air exposure, although it is exposed to the air for a few seconds before being placed in the device.

5.3 Results and Discussion

5.3.1. Effect of TiH_2 Addition to MgH_2 Electrode

Charge-discharge data were acquired from samples **1** and **2** to investigate the effects of incorporating TiH_2 in the MgH_2 electrode (Fig. 5-1(a) and 1(b)). Samples **1** and **2** exhibited initial charge (lithiation) capacities (calculated based on weight of MgH_2) of 1900 (about 121 mAh/g contributed by TiH_2 , which is calculated from capacity corresponding to the slope at 0.3 V~0.55 V in the discharge curve) and 1510 mAh/g, respectively. Both of sample **1** and sample **2** exhibited high reversibility with an initial coulombic efficiency of 94% and 97%. The former material showed more efficient utilization of MgH_2 , indicating that the addition of TiH_2 enhanced the reaction kinetics and promoted the reaction of MgH_2 in the electrode. The plateaus at 0.5 V and the slopes below 0.4 V in the charge-discharge plots for sample **1** are attributed to the reaction between MgH_2 and TiH_2 in the electrode. The data

in Fig. 5-1(e) demonstrate that charge capacities of 1700 mAh/g (equivalent to a capacity retention of 95%) and 870 mAh/g (a capacity retention of 59%) were obtained from samples **1** and **2**, respectively, after 15 cycles. It should be noted here that the volume-based proportions in the MgH_2 /electrodes used in samples **1** and **2** were almost identical. It is evident from these results that the addition of TiH_2 improved the cycling performance of the device. This effect was tentatively attributed to reductions in particle deformation stemming from the more uniform distribution of the MgH_2 electrode reaction based on improved kinetics due to TiH_2 addition. However, the capacity of sample **1** decreased significantly after 23 cycles and a capacity of only 849 mAh/g was observed after the 45th cycle, even with the addition of TiH_2 (Fig. 5-1(e)). Notably, the slope below 0.4 V also disappeared after 30 cycles, indicating that the electrochemical activity of the TiH_2 was decreased to the extent that the TiH_2 was unable to react with Li ions. Then, the capacity of MgH_2 decreased significantly without the promotion of TiH_2 . It was considered that the volume expansion of MgH_2 and TiH_2 degraded the TiH_2 interface and interrupted the solid-solid contact, which resulted in capacity degradation. Therefore, limiting volume changes of the active material and

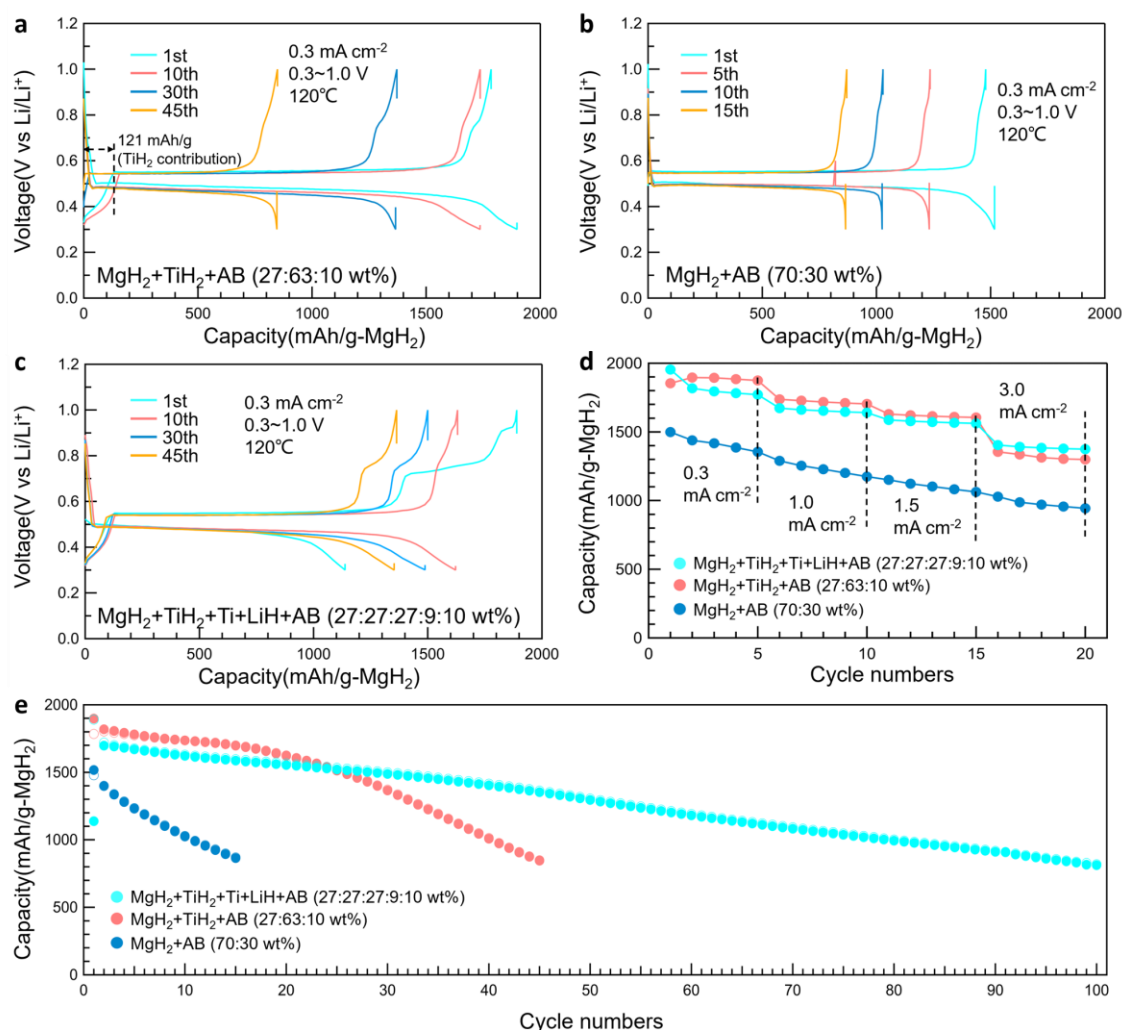


Figure 5-1. (a) Charge–discharge plots (prior rest time: 4 h) obtained at a current density of 0.3 mA cm⁻² over the voltage range of 0.3 to 1.0 V for sample **1** (MgH₂:TiH₂:AB = 27:63:10 wt%), (b) charge–discharge plots (prior rest time: 4 h) for sample **2** (MgH₂:AB = 70:30 wt%), (c) charge–discharge plots (prior rest time: 4 h) for sample **3** (MgH₂-TiH₂-Ti-LiH-AB = 27:27:27:9:10 wt%), (d) rate performance data and (e) cycling stability data for samples **1**, **2** and **3**.

creating an intimate contact region were both beneficial in terms of improving cycling performance.

Previous work confirmed that MgH₂ and Ti can react to generate Mg and TiH₂ *in situ*.^[21] The interface produced between TiH₂ and MgH₂ in this manner likely becomes more intimate and denser due to H⁻ exchange

between the MgH_2 and Ti. The charge-discharge plots acquired from sample **3** are presented in Fig. 5-1(c). After adding Ti and LiH (which reacted with Mg generated by the reaction between MgH_2 and Ti during delithiation), the cycling performance was greatly improved, and a high capacity of 819 mAh/g was obtained after 100 cycles (Fig. 5-1(e)). For rate capability, the reversible capacities determined for samples **1** and **3** were 1874, 1703, 1605 and 1299 mAh/g and 1771, 1640, 1561 and 1374 mAh/g at current densities of 0.3, 1.0, 1.5 and 3.0 mA/cm^2 , respectively (Fig. 5-1(d)). Compared with sample **1**, even with a smaller amount of added TiH_2 , sample **3** still exhibited rate performance comparable to that of sample **1**. The long plateau at 0.7 V that is apparent in Fig. 5-1(c) is discussed in the following section.

EIS analyses of the electrodes were used to investigate the effect of TiH_2 addition on reaction kinetics, working within the frequency range from 1 MHz to 0.1 Hz. The impedance plots obtained from the different electrodes (Fig. 5-2(a, b, c)) in the initial state each comprised a straight line corresponding to the Warburg resistance (related to the semi-infinite diffusion for the planar electrode), indicating low resistance in the charge transfer process. This result was in agreement with data obtained from previous research regarding anodes using LiBH_4 as the electrolyte.^[25] In the case of sample **2** (Fig. 5-2(e)), additional cycling produced charge transfer resistance that increased significantly as the number of cycles was increased.

The equivalent circuit are shown in Fig. 5-3, the charge transfer resistance can be experimentally divided into two parts of counter electrode resistance and working electrode resistance. According to previous study, the resistance related to the Li counter electrode is very small and can be neglected.^[17] The charge transfer resistance can be mainly attributed to the working electrode (anode). The Nyquist plots for sample **1** shown in Fig. 5-2(d) indicate the appearance of charge transfer resistance after five cycles along with a lower resistance than that of sample **2** after the 30th cycle. These data demonstrate that the incorporation of TiH₂ improved the reaction kinetics and decreased the resistance of anode, consistent with the charge-discharge test results. Importantly, the addition of Ti and LiH in the electrodes (Fig. 5-2(f)) did not greatly affect the Nyquist plots of sample **3**, which also exhibited a low charge transfer resistance. The Nyquist plots are consistent with the results of rate capability (Fig. 5-1(d)). Combining these results, similar to the effect of adding TiH₂, it is apparent that the reaction kinetics of sample **3** can also be enhanced by the addition of Ti and/or LiH.

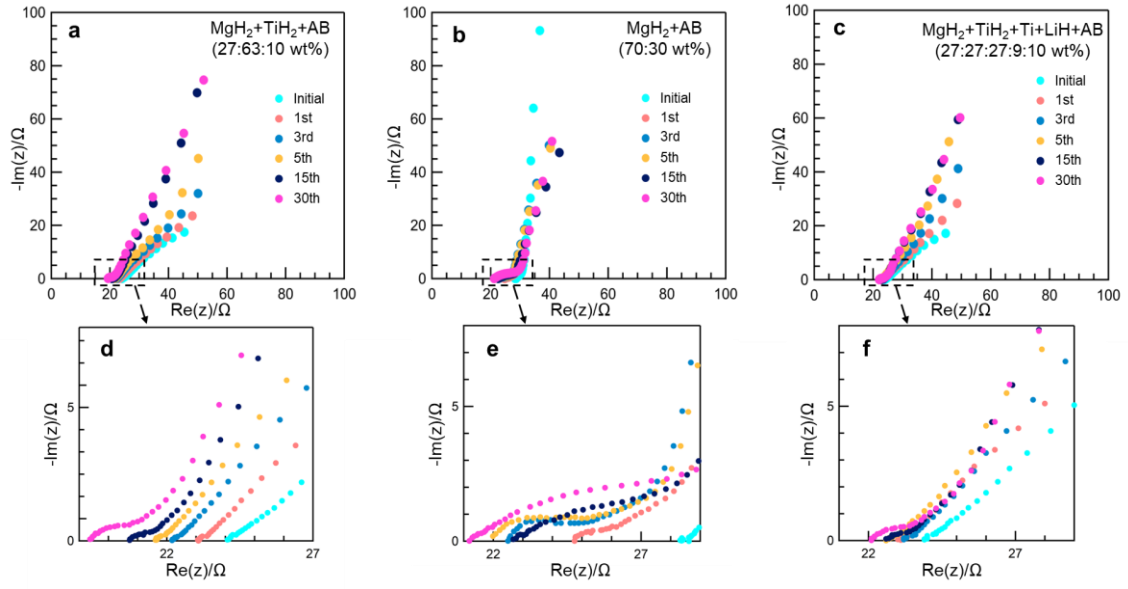


Figure 5-2. EIS plots for (a) sample 1 ($\text{MgH}_2\text{-TiH}_2\text{-AB}$ (27:63:10 wt%)), (b) sample 2 ($\text{MgH}_2\text{-AB}$ (70:30 wt%)) and (c) sample 3 ($\text{MgH}_2\text{-TiH}_2\text{-Ti-LiH-AB}$ (27:27:27:9:10 wt%)) at various charge-discharge states. (d), (e) and (f) provided magnified views of the areas enclosed by dotted lines in (a), (b) and (c).

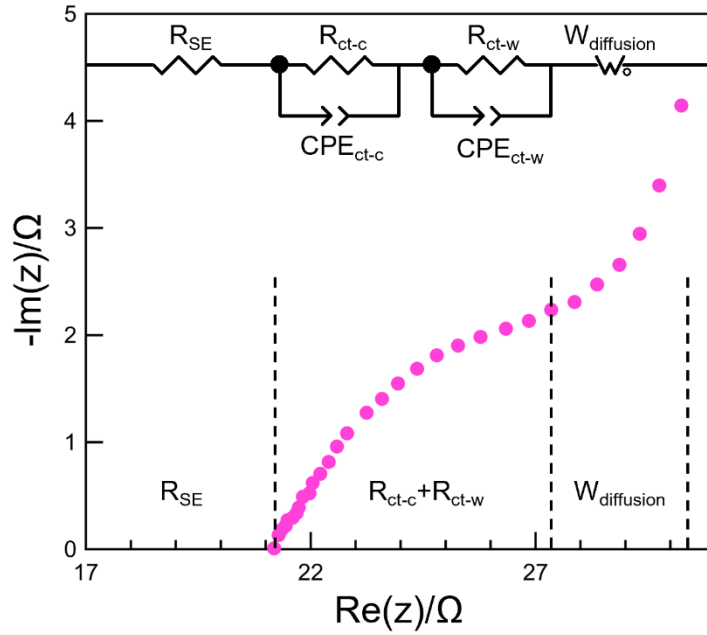


Figure 5-3. Equivalent circuit model and EIS plot for sample 2 ($\text{MgH}_2\text{-AB}$ (70:30 wt%)) after 30 cycles.

5.3.2. Mechanism for Reaction Between MgH_2 and Ti

The reaction mechanism of an electrode incorporating MgH_2 , Ti and LiH was evaluated by removing TiH_2 from the electrode composite. Electrochemical and XRD data were subsequently obtained from sample 4 (MgH_2 -Ti-LiH-AB (27:47:16:10 wt%)) in various charge-discharge states (Fig. 5-4). Compared with sample 3 (initial charge capacity: 1138 mAh/g, Fig. 5-1(c)), the initial charge-discharge curve obtained from sample 4 (Fig. 5-4(a)) shows that the charge capacity was decreased to 644 mAh/g, meaning that the reduced amount of MgH_2 reacted with the Li in this material. The XRD pattern (Fig. 5-4(b)) corresponding to the initial state contains only diffraction peaks associated with Ti and MgH_2 , indicating that no reaction occurred during the ball-milling process. The pattern acquired from the material charged to 0.3 V (Cha 0.3 V) state (equivalent to lithiation to 0.3 V) shows peaks due to $\text{TiH}_{1.5}$ at 35.8° , 41° , 59° and 70.5° , indicating that $\text{TiH}_{1.5}$ was generated *in situ* during the charging process or the rest period before the lithiation. The peaks corresponding to MgH_2 at $2\theta = 35.75^\circ$, 39.9° and 54.64° disappeared even in the case that the charge capacity was only 644 mAh/g (as compared with a theoretical capacity of 2036 mAh/g). The intensity of the Ti peak also decreased, confirming that $\text{TiH}_{1.5}$ may have been formed via the reaction between MgH_2 and Ti, in agreement with previous

work.^[21] After discharging to 125 mAh/g (Dis 125 mAh/g) there were no significant differences relative to the Cha 0.3 V state. When sample 4 was discharged to 0.7 V (Dis 0.7 V), the intensity of the Mg peaks decreased and the peaks corresponding to MgH_2 reappeared, suggesting that the plateau at 0.5 V can be attributed to the MgH_2 electrode reaction. The increased capacity associated with delithiation is ascribed to the increased proportion of Mg resulting from the reaction between Ti and MgH_2 . After further delithiation to 1.0 V (Dis 1.0 V), with the exception of peaks related to LiBH_4 in the electrolyte layer, only peaks resulting from TiH_2 and MgH_2 were obtained. The MgH_2 peaks were also more intense relative to those produced

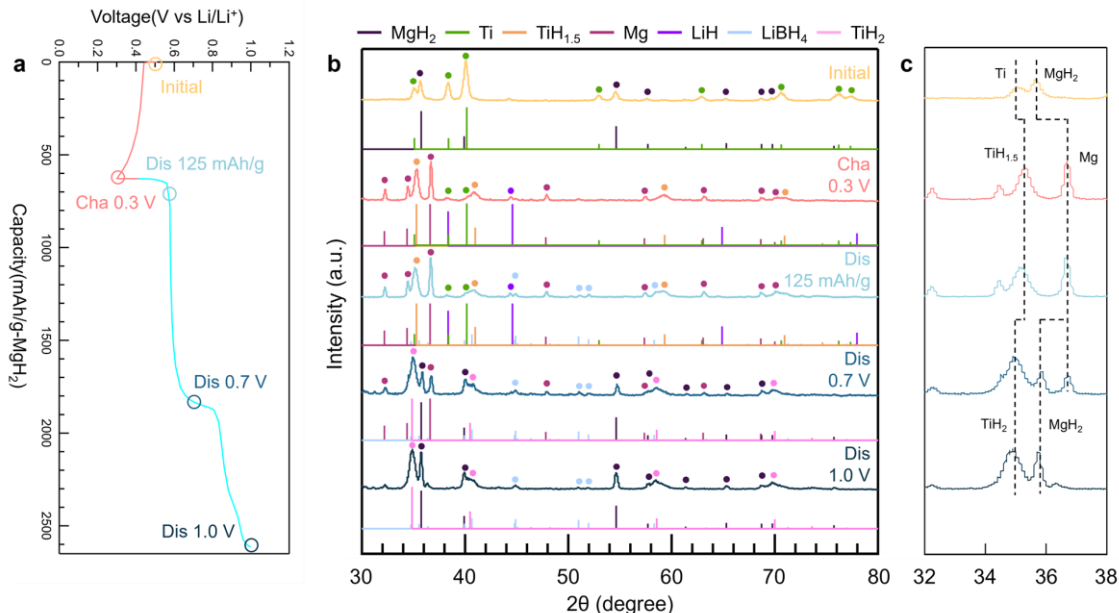


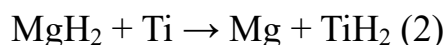
Figure 5-4. (a) Initial charge-discharge plot (prior rest time: 4 h) for MgH_2 -Ti-LiH-AB (27:47:16:10 wt%) (sample 4), (b) comparison of the *ex situ* XRD patterns for different states during initial charge-discharge cycles for the sample 4 composite electrode and (c) enlarged view of the XRD patterns. Patterns for possible products based on the ICSD are shown for reference. These include TiH_2 (ICSD: 638505), MgH_2 (ICSD: 155807), Mg (ICSD: 77908), $\text{TiH}_{1.5}$ (ICSD: 63427), Ti (ICSD: 76265) and LiH (ICSD: 61751).

by the Dis 0.7 V specimen, meaning that the plateau at 0.75 V can also be attributed to the reaction between LiH and Mg to form MgH_2 .

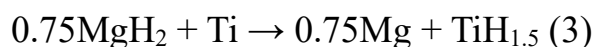
GITT data (Fig. 5-5) were obtained to further investigate the reason for the plateau at 0.75 V. Two different plateaus appeared at 0.55 and 0.75 V in the GITT plot corresponding to the delithiation process (Fig. 5-5(b)). However, the equilibrium potentials of the two plateaus were almost identical (0.5 V), indicating that the plateau occurring at the higher voltage was primarily a consequence of increased polarization. Based on the experimental evidence, the 0.75 V plateau is attributed to the reaction between Mg and the LiH that was initially manually added. This addition reduced the degree of intimate contact between the Mg and LiH such that polarization was significantly increased. In addition, the peaks corresponding to $\text{TiH}_{1.5}$ were shifted to low angles associated with TiH_2 during the delithiation process (Fig. 5-4(c)). Hence, $\text{TiH}_{1.5}$ may have undergone gradual hydrogenation through reaction with the regenerated MgH_2 .

To further investigate the mechanism of the reaction between MgH_2 and Ti, a half-cell was fabricated having a Li/LiBH₄/sample 4 structure and heated at 120 °C in an electric furnace for 65 h. XRD was used to monitor changes in the composition of the specimen following the heating process (Fig. 5-6). The XRD data demonstrated that the MgH_2 and Ti originally

present in the specimen no longer generated peaks after heating while peaks corresponding to TiH_2 and Mg appeared. This result suggested that the MgH_2 and Ti reacted to form Mg and TiH_2 *in situ* during the rest period before the charge-discharge step. In addition, compared with the Cha 0.3 V state (Fig. 5-4(b)) (meaning after a 4 h heating process), the Ti in this sample was hydrogenated to TiH_2 not to $\text{TiH}_{1.5}$. This finding suggests that the hydrogenation and dehydrogenation of Ti and MgH_2 progressed with prolonged heating. Therefore, the reaction between MgH_2 and Ti was



or



in the case that the amount of MgH_2 and/or the reaction time was insufficient. This outcome is identical to the results obtained from a previous study.^[21] Charge-discharge trials employing different heating times were also performed to obtain further information (Fig. 5-7). The lithiated capacity values for sample 4 above 0.3 V after 4, 15 and 60 h of heating were 271, 150 and 70 mAh/g, respectively. The capacity therefore decreased with increases in heating time, reflecting decreases in the amount of MgH_2 reacted with Li ions. This result is consistent with the XRD data (Fig. 5-6). The plateau at 0.15 V was attributed to the reaction between TiH_2 and Li ions. Here, it is of interest to consider the possibility that the electrode reaction of

MgH₂ and the reaction between MgH₂ and Ti occurred simultaneously. GITT trials were also performed in conjunction with the lithiation process (Fig. 5-5(c)). The voltage obviously decreased during the relaxation time (with a current density of 0 mA/cm²) as a consequence of the reaction between MgH₂ and Ti. In addition, a lower specific capacity was obtained (Fig. 5-5(a)) than that of the electrode without a relaxation time (Fig. 5-4(a)) and no additional plateaus were observed in the charge plots when the current was loaded (Fig. 5-5(a)). Combining these results, it appears that the reaction between MgH₂ and Ti occurred primarily during the relaxation time and not during the lithiation process.

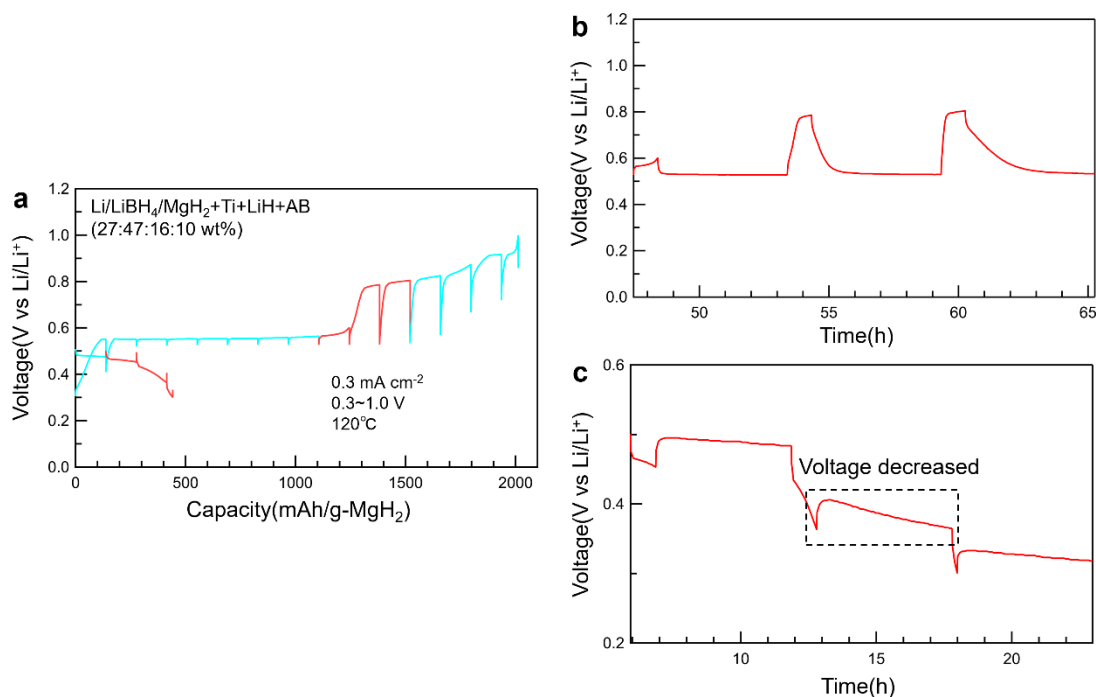


Figure 5-5. (a) GITT profiles (prior rest time: 4 h) for MgH₂-Ti-LiH-AB (27:47:16:10 wt%) composite electrode acquired at 0.8 C (0.224 mAh) with loading at 0.3 mA cm⁻² during each charge/discharge process and relaxation time of 5 h. Expanded plots showing (b) delithiation and (c) lithiation processes.

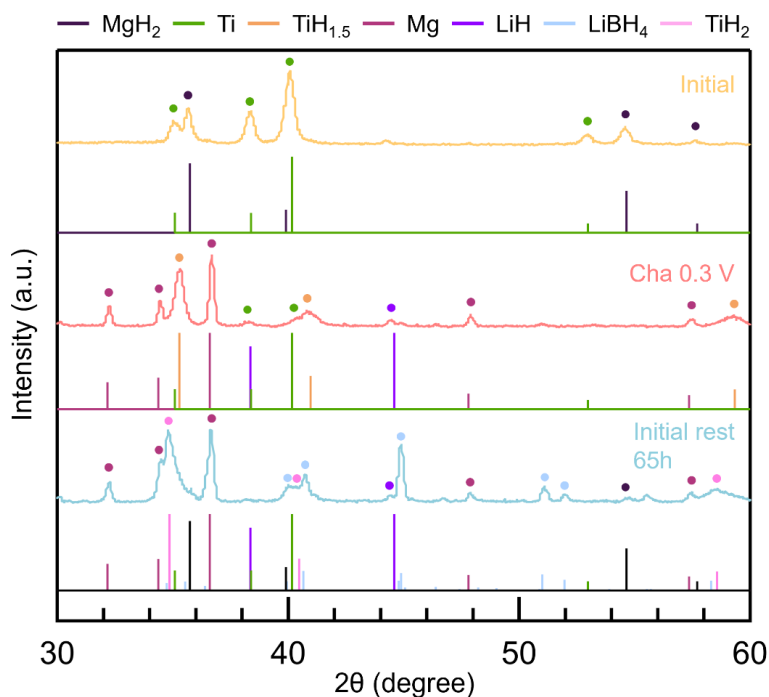


Figure 5-6. XRD patterns for $\text{MgH}_2\text{-Ti-LiH-AB}$ (27:47:16:10 wt%) electrode composite with rest time of 65 h at 120 °C.

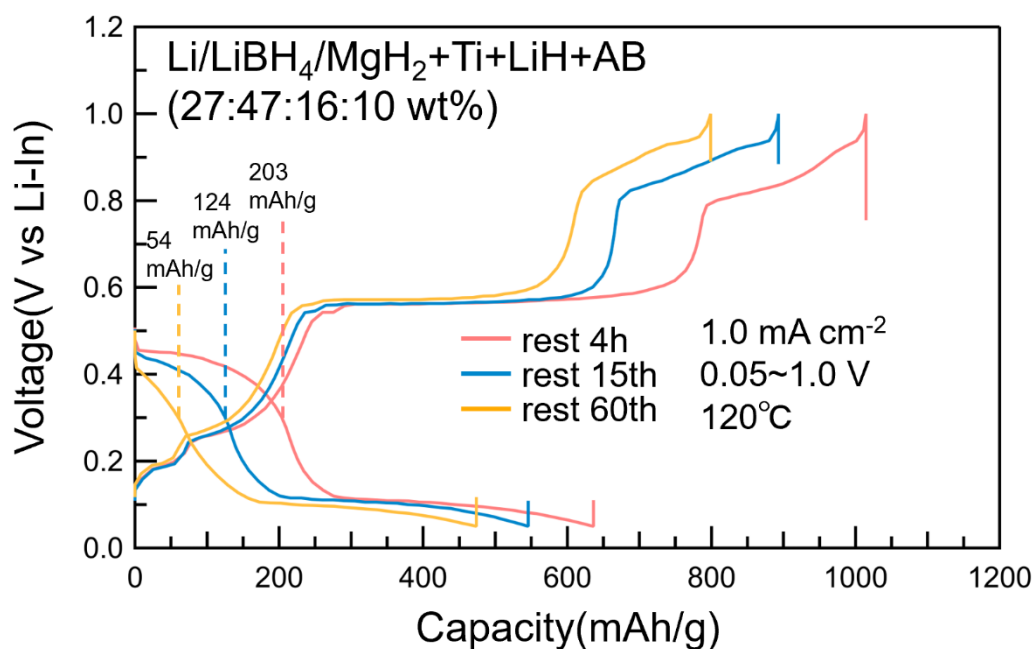


Figure 5-7. Charge-discharge voltage plots for $\text{MgH}_2\text{-Ti-LiH-AB}$ (27:47:16:10 wt%) electrode composite after various rest times prior to charge-discharge analyses.

SEM was used to investigate variations in morphology between samples **1** and **4** in the initial and delithiated states. In the initial state, the MgH_2 particle sizes were less than $3\ \mu\text{m}$ and were similar in both materials (Fig. 5-8(a) and (d)). Compared with the TiH_2 in sample **1**, the Ti particles in sample **4** were larger, likely reflecting the different particle sizes of the starting materials and/or the higher hardness of Ti. No visible differences were observed in the interfaces between the MgH_2 and $\text{TiH}_2(\text{Ti})$. After a single charge-discharge cycle from 0.3 to 1.0 V, there were no significant changes in the interface and particle size of sample **1** (Fig. 5-8(a) and (b)), indicating that no reaction occurred between the MgH_2 and TiH_2 . However, in the case of sample **4**, the electrode density increased and voids in the active material particles (such as those seen in sample **1**) disappeared following the delithiation process (Fig. 5-8(e)). Compared with the initial state of sample **4** (Fig. 5-8(d)), the electrode density was increased, and an intimate interface was obtained, as can be seen from the SEM image of sample **4** after a 15 h rest at $120\ ^\circ\text{C}$ (Fig. 5-9). These results confirm that, even at a current density of $0\ \text{mA}/\text{cm}^2$, the reaction between MgH_2 and Ti can *in situ* generate intimate interfaces between particles to increase the density of the electrode and promote the electrode reaction. Consequently, the volume change during the charge-discharge process was restricted and became more uniform. A closer analysis of Fig. 5-8(c) and (f), which provide magnified views of the area

delineated by dotted lines in Fig. 5-8(b) and (e), shows noticeable gaps between TiH_2 and MgH_2 particles in sample **1** (Fig. 5-8(c)), indicating poor solid-solid contact. In the case of sample **4** (Fig. 5-8(f)), the interface between the MgH_2 and the TiH_2 generated *in situ* is extremely intimate and no such gaps are present. The illustration of reaction mechanism of sample **4** was shown in Fig. 5-8(g). Therefore, mechanical support from the intimate interface appears to have inhibited the volume change of the TiH_2 , thereby maintaining the electrochemical activity of TiH_2 and improving the cycling performance of the electrode. The intimate contact between the MgH_2 particles is also thought to supply mechanical support to limit the maximum stress experienced by MgH_2 particles, and thus reduce cracks within the particles.

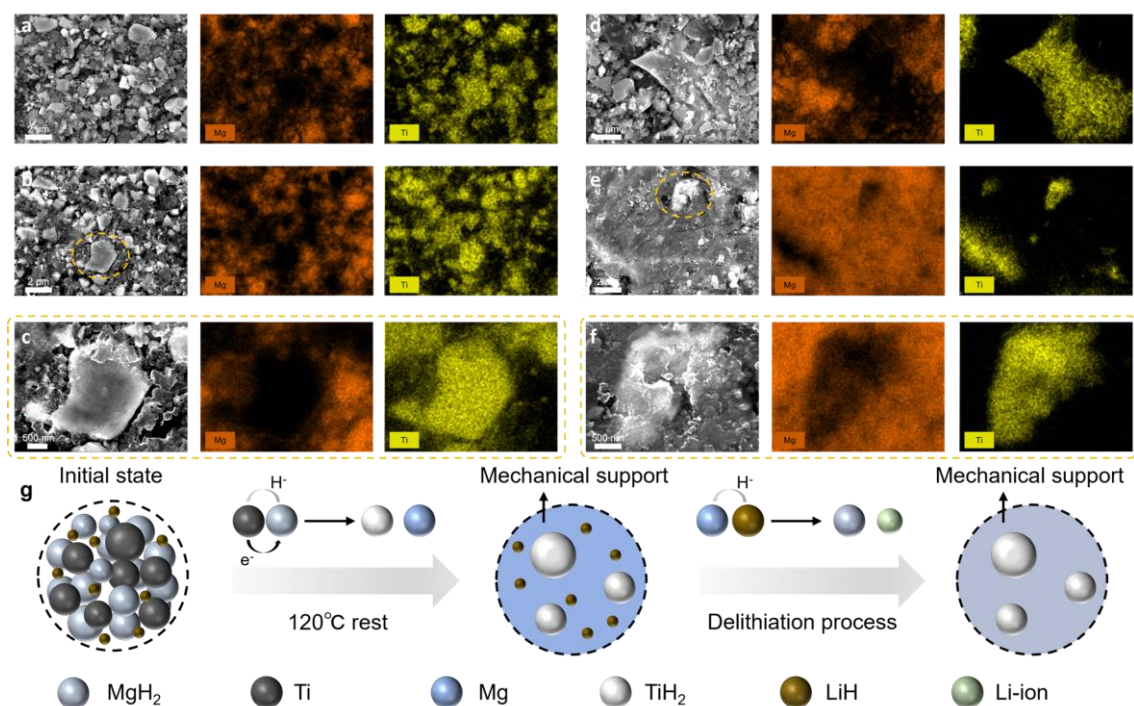


Figure 5-8. SEM images and corresponding Mg and Ti elemental maps for sample **1** (MgH₂-TiH₂-AB (27:63:10 wt%)) in (a) initial state and (b) delithiated state (voltage range: 0.3 to 1.0 V) and for sample **4** (MgH₂-Ti-LiH-AB (27:47:16:10 wt%)) in (d) initial state and (e) delithiated state (voltage range: 0.3 to 1.0 V). (c) and (f) provided magnified views of the areas enclosed by dotted lines in (b) and (e). (g) Illustration of reaction mechanism of sample **4** (MgH₂-Ti-LiH-AB (27:47:16:10 wt%)).

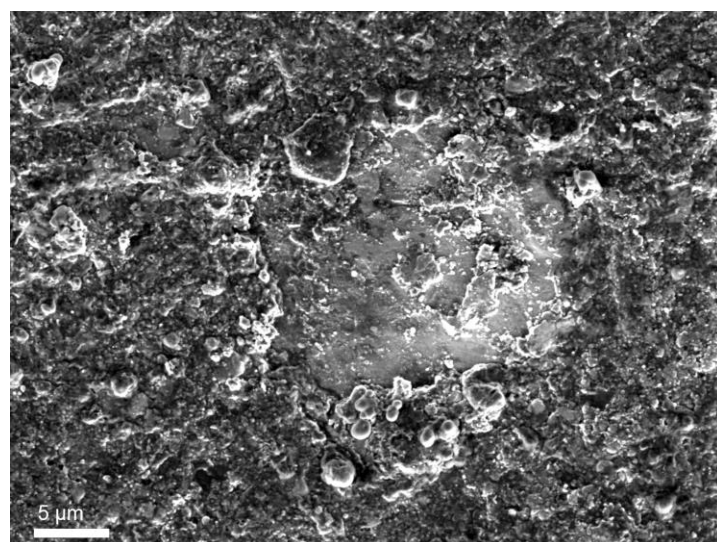


Figure 5-9. SEM image of sample **4** (MgH₂-Ti-LiH-AB (27:47:16:10 wt%)) following 15 h rest at 120 °C.

5.3.3. Enhanced Electrochemical Performance due to the *in situ* Formation of Interfaces

Electrochemical measurements were conducted to investigate the enhancement of charge-discharge performance (Sample 4) by the *in situ* formation of intimate interfaces. Sample 1 was also evaluated as comparison over the voltage range of 0.05 to 1.0 V with the results presented in Fig. 5-10. The galvanostatic discharge and charge plots obtained from sample 1 (Fig. 5-10(a)) show that an initial charge capacity of 997 mAh/g could be obtained with a current density of 1.0 mA/cm². The capacities associated with the MgH₂ and TiH₂ were determined to be 1970 and 580 mAh/g, respectively. Upon charge-discharge cycling, the specific capacity rapidly decreased to only 641 mAh/g after 50 cycles, indicating poor cycling performance and minimal stability of the artificially incorporated TiH₂. In contrast, the data for sample 4 (Fig. 5-10(b)) demonstrate that, even though the initial charge capacity was only 636 mAh/g because MgH₂ was consumed during the rest period, a high specific capacity of 896 mAh/g was recorded after 50 cycles. The plateau at 0.8 V observed in the initial discharge curve disappeared following the second because the majority of the LiH was formed by electrode reactions. In addition, it should be noted that the capacity was calculated assuming an active material content of 90 wt%, which is much

higher than the proportions typically employed in ASSBs.^[26–28] These results indicate that the *in situ* formed TiH_2 successfully worked without solid electrolyte included in electrode and exhibited high electrochemical activity after charge-discharge cycling; hence, the electrode reaction of MgH_2 can be continuously promoted by TiH_2 , delivering excellent cycling performance. The rate performance results in Fig. 5-10(c) establish that sample 4 provided reversible capacities of 1140, 961, 895 and 838 mAh/g at current densities of 0.5, 1.0, 1.5 and 2 mA/cm², respectively. When the current density was reduced back to 0.5 mA/cm², a high specific capacity of 975 mAh/g was retained, confirming the ability of sample 4 to tolerate rapid charge and discharge processes. These results suggest that the cycling stability and rate capability of sample 4 with intimate interfaces can be ascribed to the

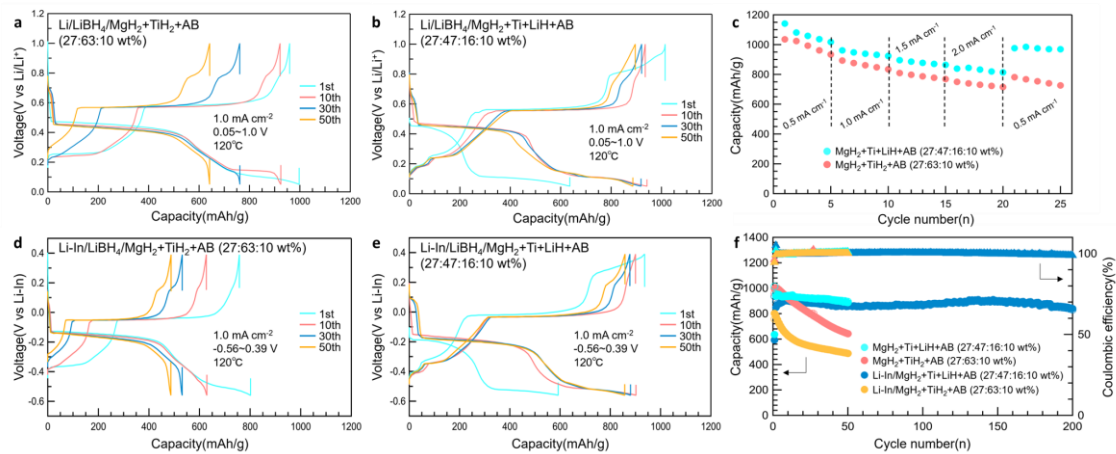


Figure 5-10. Charge–discharge profiles (prior rest time: 4 h) obtained at a current density of 1.0 mA cm⁻² and voltage range of 0.3 to 1.0 V for (a) sample 1 ($\text{MgH}_2\text{:TiH}_2\text{:AB} = 27\text{:}63\text{:}10$ wt%) and (b) sample 4 ($\text{MgH}_2\text{:Ti:LiH:AB} = 27\text{:}47\text{:}16\text{:}10$ wt%). (c) Rate performance data for samples 1 and 4. Charge–discharge plots (prior rest time: 4 h) generated using a Li-In counter electrode with a current density of 1.0 mA cm⁻² over the voltage range of -0.56 to 0.39 V for (d) sample 1 and (e) sample 4. (f) Data indicating the cycling abilities of samples 1 and 4.

inhibition of volume expansion by mechanical confinement.

Considering the potential enhanced battery performance that could be obtained via the conductive pathways provided by LiH, it was necessary to clarify the respective roles of LiH, MgH₂ and Ti in the electrode. Charge-discharge measurements were performed using sample **5** (Ti-LiH-AB (67.5:22.5:10 wt%)), sample **6** (MgH₂-LiH-AB (67.5:22.5:10 wt%)) and sample **7** (MgH₂-Ti-AB (27:63:10 wt%)) (Fig. 5-11). In the case of the electrodes that included LiH, both samples **5** and **6** exhibited poor cycling performance, indicating that LiH did not play an essential role in improving electrochemical performance. The capacity of sample **5** can be attributed to the Li insertion/extraction effect provided by the AB.^[17] Although LiH was not incorporated in the sample **7** electrode, a high capacity of 880 mAh/g was obtained after 20 cycles, suggesting that the reaction between MgH₂ and Ti was the main cause of the improved electrochemical performance. In addition, the increased initial delithiated capacity seen in the charge curve when using sample **4** (Fig. 5-10(b)) is not seen in Fig. 5-11(c). This phenomenon indicates that the increased capacity was mainly caused by the addition of LiH, which supports the hypothesis noted above. However, short-circuiting caused by Li dendrites at high current densities would be expected to affect the electrochemical performance in addition to modifying the charge-discharge process. To avoid the formation of such dendrites, charge-

discharge trials were performed using Li-In alloy (potential compared to pure Li is 0.6 V) as the counter electrode (Fig. 5-10(d) and (e)) and excellent electrochemical performance was achieved when using a Li-In/LiBH₄/sample **4** half-cell. Although a relatively low initial capacity (592 mAh/g) was obtained because of the increased interface resistance between the LiBH₄ and Li-In alloy, sample **4** was still able to deliver a reversible capacity of 829 mAh/g after 200 cycles. In contrast, the specific capacity of sample **1** when using a Li-In counter electrode was greatly decreased, to 487 mAh/g after 50 cycles. For coulombic efficiency of Li-In/LiBH₄/sample **1**, even the cells were charged to 0.05 V, high coulombic efficiency can be achieved, which is consistent with the results of Fig. 5-1(a) (charged to 0.3 V). Regarding coulombic efficiency of Li-In/LiBH₄/sample **4**, despite the initial coulombic efficiency exceeding 100% (159%) due to the reaction between the pre-added LiH and magnesium, the subsequent cycles still exhibited extremely high Coulombic efficiency (100th cycle: 100%, 200th cycle: 99%), demonstrating the excellent reversibility of the MgH₂-Ti-LiH-AB (27:47:16:10 wt%) anode. Upon further increasing the current density to 3 mA/cm² (1C), sample **4** still exhibited a reversible capacity of 608 mAh/g after 100 cycles (Fig. 5-12), demonstrating charge-discharge at a high current density and so showing the potential for practical applications. These results again confirm that the electrochemical activity of the TiH₂ formed *in*

situ, which can continuously promote the electrode reaction of MgH_2 , was significantly improved by mechanical support from the interfaces also form *in situ*.

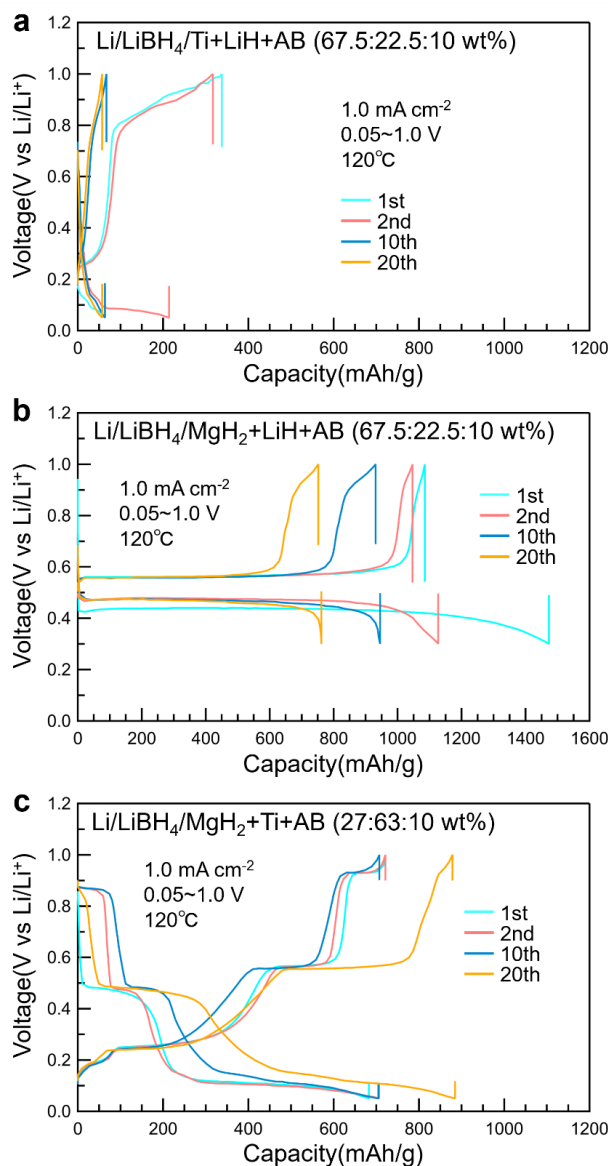


Figure 5-11. (a) Charge–discharge plots (prior rest time: 4 h) obtained at current density of 1.0 mA cm^{-2} over voltage range of 0.05 to 1.0 V for sample 5 (Ti-LiH-AB (67.5:22.5:10 wt%)), (b) charge–discharge plots (prior rest time: 4 h) for sample 6 (MgH_2 -LiH-AB (67.5:22.5:10 wt%)) and (c) charge–discharge plots (prior rest time: 4 h) for sample 7 (MgH_2 -Ti-AB (27:63:10 wt%)).

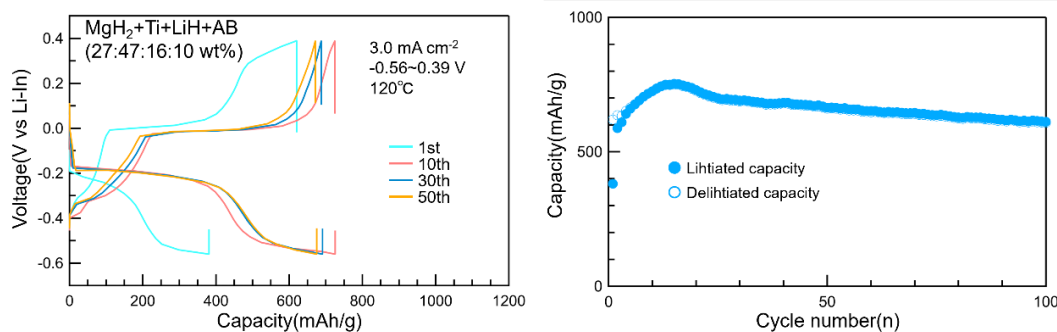


Figure 5-12. Charge–discharge voltage plots (prior rest time: 4 h) for Li-In/LiBH₄–MgH₂–Ti–LiH–AB (27:47:16:10 wt%) half-cell with current density of 3 mA/cm² (1C).

To better understand the effect of morphology on the electrochemical performance of samples **1** and **4**, SEM images (Fig. 5-13) were obtained during cycling. The images of sample **1** after 30 cycles show numerous voids and pores in the electrode due to the volume changes of the active materials (Fig. 5-13(a) and (b)). The magnified image in Fig. 5-13(b) shows voids with diameters ranging from 3 to 10 μm . These voids would not only limit contact between the MgH_2 and TiH_2 but also impede the conduction of electrons and Li ions, resulting in increased interface resistance and affecting the charge-discharge characteristics of the battery. In contrast, for sample **4**, the compact contact at the interfaces between active materials generated *in situ* was preserved during 30 charge-discharge cycles (Fig. 5-13(e, f)). No obvious voids are apparent in sample **4**, although some cracks can be observed in the enlarged images (Fig. 5-13(f)). This outcome can be attributed to the

suppressed volume change and reduced maximum stress experienced by the active particles due to mechanical support. The improved MgH_2 kinetics provided by *in situ* formed TiH_2 led to a more uniform distribution of volume change and reduced the deformation of the active material particles. The intimate interface between the MgH_2 and TiH_2 not only enhanced the kinetic performance of the MgH_2 but also limited volume expansion of the active materials (MgH_2 and TiH_2), resulting in excellent cycling stability and rate capability.

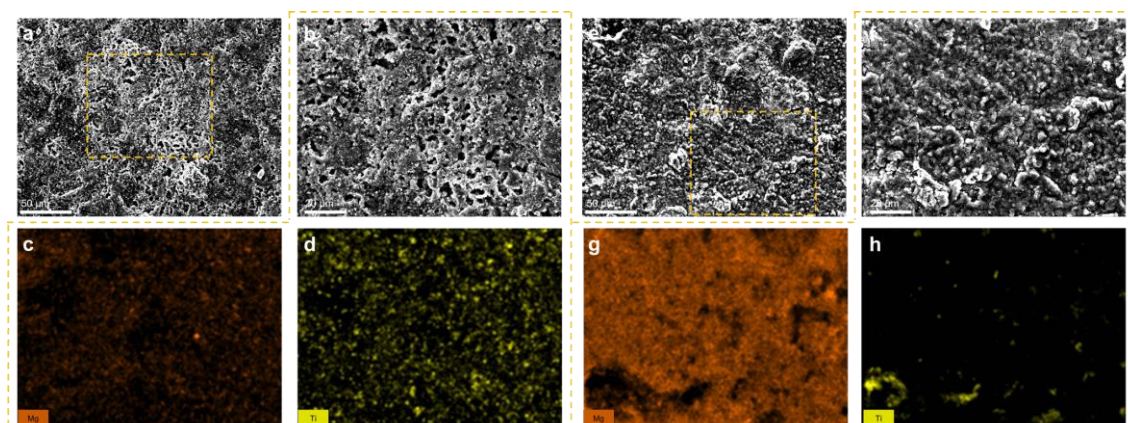


Figure 5-13. SEM images of (a) sample 1 (MgH_2 - TiH_2 -AB (27:63:10 wt%)) and (e) sample 4 (MgH_2 -Ti-LiH-AB (27:47:16:10 wt%)) after 30 cycles (voltage range: 0.05 to 1.0 V). (b) Magnified images and corresponding (c) Mg and (d) Ti mapping images of the areas enclosed by dotted lines in (a). (f) Magnified images and corresponding (g) Mg and (h) Ti mapping images of the areas enclosed by dotted lines in (e).

5.3.4. Conclusions

This work demonstrated that TiH_2 can enhance the reaction kinetics of MgH_2 , thereby improving the utilization and cycling stability of the latter. The volume changes for TiH_2 during cycling normally lead to a gradual loss of electrochemical activity, resulting in significant capacity decay. However, the present charge-discharge testing and XRD analyses confirmed that TiH_2 can be formed *in situ* within the electrode through the reaction between MgH_2 and Ti. SEM observations revealed that tightly compacted interfaces were formed between the active materials by this reaction. These interfaces promoted the electrode reaction and provided a more uniform volume change distribution that reduced deformation of the active material. The mechanical support provided by this intimate interface effectively restricted volume changes of the active materials by reducing the maximum stress. Therefore, the decay rate of the active material was limited and cycling performance was greatly improved. When using Li-In as the counter electrode, the MgH_2 -Ti-LiH-AB cell could be cycled 200 times with a current density of 1.0 mA/cm^2 and a high active material loading of 90 wt% while maintaining a high capacity of 829 mAh/g . Even at an ultra-high current density of 3 mA/cm^2 (1C), a capacity of 608 mAh/g was obtained after 100 cycles. Furthermore, according to SEM images acquired after cycling, intimate

contact between the active materials was maintained after 30 cycles. This study presents a strategy for suppressing the volume change of the active materials by mechanical support supplied by an interface formed *in situ*. This technique has the potential to promote the practical utilization of high-capacity electrodes that otherwise exhibit significant volume changes.

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Chapter 6

Conclusions

With the accelerated global transition toward decarbonization, the efficient storage and utilization of renewable energy sources such as solar and wind power have become critical for achieving carbon neutrality. As energy storage and conversion devices, batteries must prioritize two key attributes: high energy density (scalability) and safety. Unlike traditional liquid lithium-ion batteries, which face increased risks of thermal runaway as their size and capacity grow, all-solid-state lithium batteries (ASSLBs) utilize non-flammable solid electrolytes, offering significantly enhanced safety and energy density. These advantages position ASSLBs as a promising next-generation energy storage technology.

However, the development of ASSLBs is hindered by several challenges, including the fabrication of high-performance solid electrolytes, the resolution of electrode-electrolyte interface issues, and the development of high-capacity electrode materials. These challenges collectively impede the industrialization and practical application of ASSLBs. Addressing these barriers, this thesis focuses on the development of high-energy-density

anodes, proposing an innovative anode composition, using solid electrolyte *in situ* formed mechanism, that achieves a significant enhancement in anode energy density.

In Chapter 2, two new types of solid electrolyte *in situ* formed active materials were discovered. $\text{Ca}(\text{BH}_4)_2$ has been utilized as a negative electrode material in a rechargeable LIB for the first time. The results indicate that $\text{Ca}(\text{BH}_4)_2$ should be more suitable than $\text{Mg}(\text{BH}_4)_2$ for the fabrication of high voltage LIB given its lower redox potential of 0.6 V vs. Li/Li^+ . Moreover, importantly, because of the *in situ* formation of LiBH_4 during the lithiation process, no solid electrolyte component is required in the fabricated composite electrode (i.e. only the active material and activated carbon are required) and the actual capacity can be significantly improved from 170 to 331 mAh g^{-1} . Meanwhile, MgH_2 was also verified as the solid electrolyte *in situ* formed active material to charge-discharge even the ionic conductivity of LiH is low. MgH_2 -AB electrode exhibited a high initial specific capacity of 1738 mAh/g with a high active material content of 70 wt%.

In Chapter 3, $\text{Ca}(\text{BH}_4)_2$ and MgH_2 electrodes were thickened for improving energy density. The correlation between charge-discharge performance and electrode thickness of an active material that forms a solid electrolyte *in situ* was discussed and the reaction mechanism was

investigated. For $\text{Ca}(\text{BH}_4)_2$ battery with a thicker electrode (20 mg $\equiv$ 290 μm thickness) also cycled reversibly and showed comparable capacity to a battery with a thinner electrode (6 mg $\equiv$ 87 μm) in initial cycle, indicating an improvement in energy density. However, the cells show a substantial decrease in initial charge capacity when a MgH_2 -AB electrode with a thickness from 84 μm (6 mg) to 420 μm (30 mg) is used. In addition, the unreacted MgH_2 active material was investigated to be located near the current collector due to XPS analysis and the reacted electrode thickness was found to be limited to 90–140 μm . Combining these results, charger-discharge performance with thickened electrodes were mainly affected by the ionic conductivity of *in situ* formed electrolyte. Nonetheless, further efforts are needed to improve the energy density of batteries based on MgH_2 anode.

In Chapter 4, further effort on increasing energy density of MgH_2 electrode were done. TiH_2 was used as bifunctional material (that functions as both an active material that forms a solid electrolyte *in situ* and a conductor additive) to mix with MgH_2 . Compared with previously reported metal-hydride anodes, our MgH_2 - TiH_2 -AB electrode achieved a higher energy density, even when the AB content of the electrode was 10 wt%, indicating the feasibility of using TiH_2 as the conductor additive. Moreover, when VGCF was substituted for AB as the carbon additive, remarkable improvements in the charge-

discharge performance (initial lithiation capacity: 1342 mAh/g (electrode utilization ratio: 86%)) and energy density (increase in volumetric energy density from 1977 Wh/L (AB) to 2153 Wh/L (VGCF)) were attained as a result of continuous electron pathways provided by the VGCF;

The results showed that the TiH_2 bifunctional material not only enables smaller amounts of solid electrolytes and carbon additives to be used in the electrode composites but also exhibits a high capacity and low potential. I believe this material will play a critical role in the development of high-energy-density negative electrode materials with a high active material content for practical use in ASSBs.

In Chapter 5, based on the anodes, with high energy density, described in Chapter 4, a metal hydride anode with improved cycling performance and higher rate performance has been developed, through spontaneous densification of electrode. SEM observations revealed that tightly compacted interfaces were formed between the active materials by reaction between MgH_2 and Ti. These interfaces promoted the electrode reaction and provided a more uniform volume change distribution that reduced deformation of the active material. The mechanical support provided by this intimate interface effectively restricted volume changes of the active materials by reducing the maximum stress. Therefore, the decay rate of the active material was limited and cycling performance was greatly improved. When using Li-In as the

counter electrode, the MgH₂-Ti-LiH-AB cell could be cycled 200 times with a current density of 1.0 mA/cm² and a high active material loading of 90 wt% while maintaining a high capacity of 829 mAh/g. Even at an ultra-high current density of 3 mA/cm² (1C), a capacity of 608 mAh/g was obtained after 100 cycles.

In conclusion, this thesis successfully developed a metal hydride anode for all-solid-state batteries (ASSBs) with a high active material content of 90 wt% using a solid electrolyte and *in situ* interface formation method. The anode exhibited excellent cycling performance even under high current density conditions. This research has the potential to guide the development of high-capacity anodes and promote the practical utilization of ASSBs.

To enable the practical application of solid electrolyte *in situ* formed anodes in all-solid-state batteries, at least three issues need to be addressed. The first is the reduction in operating temperature. For ensuring that the battery performs well at room temperature, using active material which can form solid electrolyte with high ionic conductivity at room temperature is necessary. The second is achieving better cycling performance. A capacity retention of over 80% after 1000 cycles is required to surpass the performance of existing liquid-based batteries. The third issue is improving the interface compatibility with high-performance electrolytes such as sulfides. For the commercialization of solid-state batteries, the

electrode/solid electrolyte interface remains a key challenge. These topics will continue to be researched in the future.

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