Electrochemical Performance of Titanium Hydride for Bulk-Type All-Solid-State Lithium-Ion Batteries

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TiH₂ was utilized as a negative electrode material for lithium ion battery by using LiBH₄ solid electrolyte. High reversibility of the TiH₂ conversion reaction was successfully obtained in this work. The favorable electrochemical properties of TiH₂ electrode such as robust cyclic and rate performances were reported for the first time, which are superior to the previous report by means of conventional organic liquid electrolyte system. It can be considered as a promising candidate as negative electrode for lithium-ion batteries.

Keywords: lithium ion battery, conversion reaction, hydride anode, solid state electrolyte, lithium borohydride, titanium hydride

1. Introduction

Metal hydrides, which are mainly considered as hydrogen storage materials, have been studied as conversion-type negative electrode materials for lithium-ion batteries (LIBs) in recent years, owing to their high theoretical Li storage capacities, relatively low volume expansions and suitable working potentials. The Li⁺ insertion/extraction reactions for metal hydrides can be written by the following hydride conversion reaction:

$$MH_x + xLi^+ + xe^- \leftrightarrow M + xLiH.$$  (1)

Among all of the metal hydrides, MgH₂ shows the most promising electrochemical performance due to its high theoretical capacity of 2038 mAh g⁻¹, which has been intensively studied by many research groups¹–⁸. Another promising candidate of metal hydrides as negative electrode is titanium hydride (TiH₂), which has a theoretical capacity of 1074 mAh g⁻¹ with a low working potential of 0.163 V versus Li⁺/Li. The following reaction:

$$TiH_2 + 2Li^+ + 2e^- \leftrightarrow Ti + 2LiH.$$  (2)

In the viewpoint of high power battery, TiH₂ is preferable to MgH₂ as negative electrode since its theoretical working potential is much lower than MgH₂, which leads to a higher voltage for a full battery cell. The electrochemical Li insertion/extraction mechanism of TiH₂ was reported by Oumellal et al.⁹,¹⁰. However, the cycle properties have not been reported yet due to the poor reversibility in conventional organic liquid based electrolyte.

In this paper, we prepared the TiH₂–LiBH₄ composite as the negative electrode together with LiBH₄ as the solid-state electrolyte for an all-solid-state battery cell, in order to obtain good cyclic performance for TiH₂. This system is similar to our previous study for MgH₂ electrode, which showed favorable electrochemical performances¹¹. The phase evolution of TiH₂ electrode upon charge-discharge in the solid-state cell, cyclic properties and rate performance are investigated in this study.

2. Experimental Procedure

As starting materials, TiH₂ powder (98%, Sigma-Aldrich), LiBH₄ powder (≧95%, Sigma-Aldrich), acetylene black, lithium metallic disc (99.8%, Honjo Metal) were obtained commercially. Firstly, composite electrodes were prepared by mechanical ball-milling method. The active materials of TiH₂ were weighted to be 300 mg, and placed into Cr-steel ball-milling pot (volume of 30 mL) with 20 zirconia balls (diameter of 8 mm). After that, the samples were mechanically milled for 20 h with 370 rpm by a planetary ball-milling apparatus (Fritsch P7). Then, the active materials were loaded into ball-milling pot together with LiBH₄ as solid electrolyte¹² and acetylene black as electro-conducting material in a weight ratio of 40:30:30 having a total amount of 200 mg. The mechanical milling was conducted for 2 h to synthesize homogeneous composite electrode. The all-solid-state cells were fabricated by the following processes. Li metallic disc and LiBH₄ solid electrolyte were pressed together under 360 kg cm⁻². Then, the obtained composite electrode was placed on the LiBH₄ side and pressed under 1450 kg cm⁻². The three-layered bulk was placed in the coin cells (2032 type, Hohsen Corp.) sealed with PFA gasket.

Galvanostatic charge-discharge measurements were conducted by charge-discharge analyzer (HJ1001SD8, Hokuto Denko Co.) at 120°C in which the LiBH₄ solid electrolyte showed high ionic conductivity. To keep the temperature and prevent air exposure, oil bath was used as heat source. To characterize the structural properties of composite electrode, ex-situ XRD measurement (RINT-2100, Rigaku) was performed using Cu-Kα radiation at room temperature. Since the composite electrode was sensitive to moisture, all ex-situ XRD measurements have been conducted under Ar atmosphere sealed with poly-imide film (Kapton, DuPont-Toray Co., LTD.).
3. Result and Discussions

Figure 1 shows the initial charge-discharge curves of the TiH₂ electrode using LiBH₄ solid electrolyte with the voltage window between 1.0 V and 0.05 V under the current density of 400 mA g⁻¹ at 120°C. The Li insertion curve shows slope (0.4 V–0.15 V) and plateau (0.15 V) regions. From the previous report¹⁰, it was considered that the slope region indicated fcc-TiH₂ reacted with lithium to form LiH and partially transformed into a distorted orthorhombic phase fco-TiH₂ₓ, and plateau region indicated that both of fcc-TiH₂ and fco-TiH₂ₓ react with lithium to form Ti and LiH as shown by reaction (2). Unlike the case of MgH₂, no plateau was observed below 0.15 V, indicated Ti didn’t electrochemically react with Li to form Li-Ti alloy. During the initial Li insertion, the capacity of 1225 mAh g⁻¹ was obtained, while the theoretical capacity was 1074 mAh g⁻¹. This overcapacity could be due to the existence of acetylene black in the electrode, which contributes on the Li storage capacity as an anode.

On the Li extraction curve, the plateau corresponding to de-lithiation process of TiH₂ conversion reaction was observed at higher voltages than 0.15 V, indicating the higher polarization of electrode compared with the case of MgH₂ system¹¹. Furthermore, a short plateau at 0.75 V was observed and the whole Li extraction curve showed 1052 mAh g⁻¹ corresponding to 86% coulombic efficiency. In order to identify the electrochemical reaction, ex-situ XRD measurements were performed at the different states-of-charge (i)–(v) as shown in Fig. 1. It is noteworthy that all the profiles shown in Fig. 2 contain peaks corresponding to LiBH₄, which should always be included in the electrodes. At the initial state (i), the broad peaks corresponding to TiH₂ were observed due to the ball-milling effect. After the Li insertion (ii), the broad peaks slightly shifted to higher angle, indicating that the TiH₂ structure should be slightly shrunk due to partial extraction of hydrogen. And small peaks corresponding to fco-TiH₂ₓ and Ti were observed. With further lithiation (iii), it was clearly observed that the TiH₂ changed to Ti and LiH. For the Li extraction process, H atoms were transferred from LiH to Ti. Then, as shown in Fig. 2 (iv, v), peaks corresponding to TiH₂ were reappeared, then the Ti peak was strongly reduced. These facts indicate that TiH₂ electrode reveals high electrochemical performance by using the all-solid-state cell. Actually, both of MgH₂ and TiH₂ anodes for liquid electrolyte systems haven’t shown such a high coulombic efficiency. The combination of hydride and borohydride for anode and electrolyte, respectively, could lead to a better performance.

Unfortunately, the reaction at 0.75 V as shown in Fig. 1 was not clarified yet even though we have performed the XRD measurements at various states of charge. As one of the possible reasons, it could be caused by the Li extraction process from acetylene black, which cannot be detected by XRD due to its amorphous feature.

Figure 3 shows the cyclic performance of TiH₂–LiBH₄ composite electrode in the voltage range of 1.0 V–0.05 V at a current density of 400 mA g⁻¹ at 120°C. Almost the same profile as the initial cycle was observed in later cycles. The Li insertion capacities of the 2nd, 10th, and 50th cycles were 1094, 1035 and 878 mAh g⁻¹, respectively. Corresponding capacity retention after the 50th charge-discharge cycles of about 80% for this TiH₂-LiBH₄ system is much better than that of about 50% for the previous MgH₂-LiBH₄ system¹¹. This result revealed for the first time that the charge-discharge process of TiH₂ electrode is recyclable, which makes it a promising candidate for lithium-ion batteries. While the reason of the 20% degradation after 50 cycles could be due to mechanical factor such as agglomeration of Ti species and/or detachment due to volume expansion, for a practical utilization, the detailed mechanism should be clarified as further research.

The rate capability of the TiH₂ composite electrode was

![Fig. 1](image1.png)  
Fig. 1 First galvanostatic charge-discharge curves for TiH₂–LiBH₄ electrode in the voltage range of 2.0 V–0.05 V at a current density of 400 mA g⁻¹ at 120°C.

![Fig. 2](image2.png)  
Fig. 2 Ex-situ XRD patterns of TiH₂–LiBH₄ at the various states-of-charge.
also investigated as shown in Fig. 4. All the discharge profiles in this figure were created by the initial discharge cycle of independent cells at different current densities of 400, 800, and 1600 mA g\(^{-1}\), which are corresponding to about 1/3C, 2/3C, and 4/3C, respectively. It can be seen that discharge capacities were 1225, 1165 and 1007 mAh g\(^{-1}\) at the current density of 400, 800, and 1600 mA g\(^{-1}\), respectively, indicated a good rate capability of TiH\(_2\) electrode in this system. For comparison, the charge-discharge for TiH\(_2\) in a conventional organic electrolyte could be performed only at 10 mA g\(^{-1}\)\(^{13}\). The fast kinetics could be ascribed to rapid Li\(^+\) and H\(^-\) diffusion in the electrode material and on the electrode–electrolyte interface at a high working temperature of 120°C. It was noteworthy that the average voltage gradually decreased along with the increasing discharge rate, while the theoretical equilibrium potential of this conversion reaction was 0.163 V versus Li\(^+\)/Li. It was considered that the decrease of equilibrium potential could be caused by the insufficiency of electronic conductivity at high current density, which can be improved by surface modification such as carbon coating or other technique.

4. Conclusion

In summary, TiH\(_2\) was successfully performed as a negative electrode material for all-solid-state lithium-ion batteries by using LiBH\(_4\) solid electrolyte. As is similar to the previous report by using a conventional liquid electrolyte, slope and plateau regions were observed in the Li insertion curve, which are corresponding to fco-TiH\(_{2-x}\) and Ti generations, respectively. The whole Li extraction curve showed 1052 mAh g\(^{-1}\) corresponding to 86% coulombic efficiency at the initial cycle. However, even after the 50 cycles, the Li insertion capacities were kept to be 878 mAh g\(^{-1}\). Moreover, even at high current rate of 1600 mA g\(^{-1}\) corresponding to more than 1C, the discharge capacity at the initial cycle was not strongly reduced and was kept to be 1007 mAh g\(^{-1}\).

REFERENCES