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Effects of Metal Oxide Additives on Anode Properties of Magnesium Hydride for All-Solid-State Lithium Ion Batteries

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We fabricated an all-solid-state lithium ion battery with magnesium hydride (MgH_2) anode which was catalyzed by doping 5mol% Nb_2O_5 ($95MgH_2$-$5Nb_2O_5$) to increase low first-coulombic-efficiency of MgH_2 anode. The catalyzed MgH_2 ($99MgH_2$-$1Nb_2O_5$, $95MgH_2$-$5Nb_2O_5$) and solid electrolyte were independently synthesized by mechanical ball milling. In order to investigate the hydrogen desorption temperature of pristine MgH_2, $99MgH_2$-$1Nb_2O_5$ and $95MgH_2$-$5Nb_2O_5$, thermal desorption mass spectroscopy was carried out. In addition, the charge and discharge measurement for $95MgH_2$-$5Nb_2O_5$ was carried out at 100 ℃ and at current density of 0.05 mA cm^{-2} and 0.15 mA cm^{-2}. As a result, the following results were revealed. (1) The hydrogen desorption temperature decreases with increasing Nb_2O_5 contents and columbic efficiency increases with increasing Nb_2O_5 contents. Therefore, the columbic efficiency increases with decreasing hydrogen desorption temperature. (2) Rate properties of MgH_2 are also improved with increasing Nb_2O_5 contents. (3) Effect of Nb_2O_5 additives on anode properties of MgH_2 is clearer upon the Li extraction reaction than that upon the Li insertion reaction due to thermodynamically and electrochemically reasons. (4) Upon the Li insertion reaction, effect of Nb_2O_5 additives become clearer at current density of 0.15 mA cm^{-2} than that of 0.05 mA cm^{-2}.

Thus, the anode properties of MgH_2 are improved by adding Nb_2O_5.

マグネシウムハイドライド（MgH_2）の初期の低いクーロン効率を改善するために，マグネシウムハイドライドに5 mol%の五酸化ニオブ（Nb_2O_5）を添加し，これを電極とした全固体リチウムイオン電池を作製した。五酸化ニオブを1 mol%および5 mol%添加したマグネシウムハイドライド（$99MgH_2$-$1Nb_2O_5$，$95MgH_2$-$5Nb_2O_5$）並びに固体電解質はメカニカルボールミリングによってそれぞれ合成した。MgH_2，$99MgH_2$-$1Nb_2O_5$，$95MgH_2$-$5Nb_2O_5$からの水素放出温度は昇温脱離質量分析によって測定した。また，$95MgH_2$-$5Nb_2O_5$の充放電測定は，電流密度を0.05 mA cm^{-2}，0.15 mA cm^{-2}として100℃の温度条件下で行った。その結果以下が明らかとなった。(1)MgH_2の水素放出温度はNb_2O_5の添加量が増加するのにつれて低下する。また，クーロン効率はNb_2O_5の添加量が増加するのにつれて向上する。従って，クーロン効率はMgH_2の水素放出温度が低下するのにつれて向上するといえる。(2)MgH_2のレート特性もNb_2O_5を添加することによって改善する。(3)MgH_2へのNb_2O_5の添加効果は，熱力学的・電気化学的な理由からリチウム吸蔵反応よりリチウム放出反応の方が顕著になる。(4)リチウム吸蔵反応において，MgH_2へのNb_2O_5の添加効果は電流密度が0.15 mA cm^{-2}の方が0.05 mA cm^{-2}よりも顕著になる。

このように，MgH_2の負極特性はNb_2O_5を添加することによって改善する。

Key Words
Lithium-ion battery, Negative electrode, Niobium oxide, Hydrogen

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1. Introduction

Lithium ion batteries (LIBs) are vital devices for our society. The commercial LIB mostly consists of graphite (anode), organic liquid electrolyte, and lithium transition metal oxide (cathode). The capacity of graphite in current commercial LIBs achieves its theoretical capacity (372 mA h g^{-1}), so we need anode materials with high capacity for future market demands.

MgH_2 is one of promising anode materials because it has high theoretical capacity of 2038 mA h g^{-1} by the following reaction,

$$MgH_2 + 2Li^+ + 2e^- \leftrightarrow Mg + 2LiH \tag{1}$$

According to Oumella *et al.*, MgH_2 reveals large reversible capacity of 1480 mA h g^{-1} and plateau voltage at 0.5V [1]. Mg ab/desorbs hydrogen by the following reaction,

$$Mg + H_2 \leftrightarrow MgH_2 \tag{2}$$

and, MgH_2 is known as candidate of hydrogen storage material. Although it has a high hydrogen storage capacity of 7.6 mass% and Mg is abundant material, in terms of practical use, MgH_2 has disadvantageous properties due to high temperature on the hydrogen ab/desorption reaction and its slow sorption kinetics [2] [3]. Recently, it has been reported that the hydrogen sorption kinetics is improved by adding transition metal oxide or metal oxide [4] ~ [7]. In particular, Nb_2O_5 is the most effective catalyst to improve the kinetics of the hydrogen ab/desorption reaction among the other metal oxides, such as V_2O_5, TiO_2, Al_2O_3, SiO_2, and so on [8] [9]. Moreover, MgH_2 catalyzed with Nb_2O_5 was rehydrogenated even at room temperature [10] [11].

All-solid-state LIBs are safer batteries than commercial LIBs, because all-solid-state LIBs involve nonflammable solid electrolyte, which has large voltage window, instead of flammable liquid electrolyte. We fabricated an all-solid-state LIB with MgH_2 anode and investigated the Li insertion (charge) and extraction (discharge) reactions [12]. Upon the Li insertion reaction, the voltage curve showed a plateau feature located at 0.45V, and the first-charge/discharge efficiency (coulombic-efficiency) was 32%. Coulombic-efficiency is equal to mole fraction of extracted Li^+ ions divided by mole fraction of inserted Li^+ ions. Furthermore, we revealed that the catalytic effect stabilizes the plateau voltage on the anode of MgH_2 catalyzed with Nb_2O_5 ($99MgH_2$-$1Nb_2O_5$). In addition, first-coulombic-efficiency was 42%. Nb_2O_5 is the most effective catalyst to improve its slow kinetics of hydrogen ab/desorption of Mg as mentioned above. Similarly, Nb_2O_5 improved the kinetics of the electrochemical reaction by accelerating the hydrogen atoms transportation from the Mg phase to the Li phase due to decreasing activation energy of hydrogen ab/desorption of Mg. As a result, coulombic-efficiency of MgH2 was increased.

We synthesized the catalyzed MgH_2 by doping with 5 mol% Nb_2O_5 (95MgH2-$5Nb_2O_5$) to further increase first-coulombic-efficiency of MgH_2 for all-solid-state LIBs. In addition, the effect of metal oxide additives, in particular, Nb_2O_5, on the MgH_2 anode was discussed in this paper.

2. Experimental

The solid electrolyte $80Li_2S$-$20P_2S_5$ [13] was synthesized by mechanical ball-milling. The mixture of Li_2S (Furuuchi Chemistry, 99.9%) and P_2S_5 (Sigma Aldrich, 99%) with the molar ratios of 80 : 20 was put into the zirconia vessel (30 ml internal volume) with ten pieces of zirconia balls. Then, the mixture was mechanically milled for 20 h at 370 rpm under 0.1 MPa of argon gas atmosphere using a planetary ball milling apparatus (Fritsch P7). The Nb_2O_5 (Sigma Aldrich, 99.5%) doped MgH_2 (Alfa Aesar, 98%) was synthesized by mechanical ball-milling for 20h [10] [11]. The samples before and after ball milling were always handled in a glove-box filled with a purified Ar gas atmosphere (Miwa MFG). The electrode mixture of the catalyzed MgH_2 by doping with 5 mol% Nb_2O_5 solid electrolyte $80Li_2S$-$20P_2S_5$, and acetylene black was obtained by hand-milling with proper weight ratios. These electrode mixtures were pressed into 16 mm diameter tablet with $80Li_2S$-$20P_2S_5$ and lithium metal as counter electrode. Then, this tablet was placed in the experimental cell.

The charge and discharge properties were measured by galvanostat (HJ-SM8, Hokuto Denko Co.) at a voltage between 0.1V and 1.5V versus Li^+/Li, current density of 0.05 mA・cm^{-2}, and temperature of 100 ℃. The hydrogen desorption temperature of the catalyzed MgH_2 of $99MgH_2$-$1Nb_2O_5$ and $95MgH_2$-$5Nb_2O_5$ were examined by a thermal desorption mass spectroscopy (TDMS) (Anelva M-QA200TS) with heating process up to 450 ℃ and a rate of 5 ℃ min^{-1}. All the procedure was done without exposing to the air and moisture. The experimental conditions of each measurement toward pristine MgH_2, $99MgH_2$-$1Nb_2O_5$ and $95MgH_2$-$5Nb_2O_5$ were written in **Table 1**.

Table 1 Experimental conditions

	Contents of Nb_2O_5	Charge/discharge measurement	
pristine MgH_2	0 mol%	Ref. (12)	0.15mA・cm^{-2}
$99MgH_2$-$1Nb_2O_5$	1 mol%		
$95MgH_2$-$5Nb_2O_5$	5 mol%	0.05mA・cm^{-2}	

3. Results and discussion

The hydrogen desorption temperature from pristine MgH_2 and the catalyzed MgH_2 of $99MgH_2$-$1Nb_2O_5$ and $95MgH_2$-$5Nb_2O_5$ are shown in **Fig. 1**, where the notation of "0 mol%" means pristine MgH_2. The hydrogen desorption temperatures of pristine MgH_2, $99MgH_2$-$1Nb_2O_5$, and $95MgH_2$-$5Nb_2O_5$ are 410 ℃, 310 ℃ and 250 ℃, respectively. Namely, the hydrogen desorption temperature decreases with increasing Nb_2O_5 contents as follows,

$$T_{des}\ (MgH_2) > T_{des}\ (Nb_2O_5;1mol\%) > T_{des}\ (Nb_2O_5;5mol\%) \quad (3)$$

where, T_{des} (MgH_2), T_{des} (Nb_2O_5; 1mol%), T_{des} (Nb_2O_5; 5mol%) represent the hydrogen desorption temperature of pristine MgH_2, $99MgH_2$-$1Nb_2O_5$, $95MgH_2$-$5Nb_2O_5$, respectively.

The VC curves of the Li insertion and extraction reactions corresponding to the $95MgH_2$-$5Nb_2O_5$ are shown in **Fig. 2**. The horizontal axis shows mole fraction of lithium ion (x) per Mg in the electrode of $95MgH_2$-$5Nb_2O_5$. Upon the Li insertion reaction, the voltage corresponding to the $95MgH_2$-$5Nb_2O_5$ is suddenly dropped to 0.4 V at x = 0.6, and then gradually decreased to 0.1 V as a plateau-like feature upon Li^+ ions insertion of 3.2 mol into the electrode mixture. The VC curve of Li insertion corresponding to $95MgH_2$-$5Nb_2O_5$ shows similar curve to pristine MgH_2. In the case of $99MgH_2$-$1Nb_2O_5$, a clear plateau was observed in voltage located at 0.45 V between x = 0.4 and x = 2.1 with a current density of 0.05 mA cm・2 at 100 ℃. In other words, the plateau features become more stable (clearer) for the addition of Nb_2O_5, than that for no additives. This stabilization of the plateau indicated that the Nb_2O_5 catalyst for the hydrogen desorption kinetics of MgH_2 was also improved in the kinetics of the electrochemical reaction to transfer a hydrogen atom from the Mg phase to the Li phase [12]. According to TDMS profiles, the hydrogen is desorbed from $95MgH_2$-$5Nb_2O_5$ in the lower temperature region than that of $99MgH_2$-$1Nb_2O_5$. Although hydrogen desorption kinetics of MgH_2 in $95MgH_2$-$5Nb_2O_5$ was improved, the kinetics of the electrochemical reaction to transfer a hydrogen atom from the Mg phase to the Li phase seemed not to be improved due to plateau voltages. Nb_2O_5 is an insulator and exists on the surface of MgH_2, indicating that Nb_2O_5 disturb the physically direct contact between MgH_2 and acetylene black (AB). This situation offers electrical conductive path was obstructed by Nb_2O_5 with increasing contents of Nb_2O_5. This is the reason why the VC curve corresponding to $95MgH_2$-$5Nb_2O_5$ did not show any stabilization of the plateau. Upon the Li extraction reaction, both the VC curve of the $95MgH_2$-$5Nb_2O_5$ showed a plateau feature around 0.1 V and 0.6 V. When mole fraction of extracted Li^+ ions are 1.75 mol after the voltage reached 1.5 V, the plateau of the $95MgH_2$-$5Nb_2O_5$ had a larger capacity than that of the pristine MgH_2 and $99MgH_2$-$1Nb_2O_5$ [12].

Coulombic-efficiency of pristine MgH_2, $99MgH_2$-$1Nb_2O_5$, and $95MgH_2$-$5Nb_2O_5$ are shown in **Fig. 3**, where the

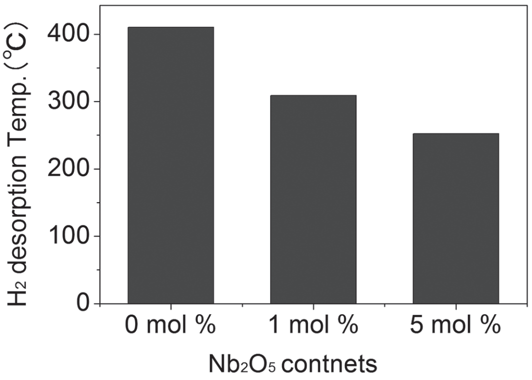

Fig. 1 Hydrogen desorption temperature from pristine MgH_2, Nb_2O_5 doped MgH_2, $99MgH_2$-$1Nb_2O_5$ and $95MgH_2$-$5Nb_2O_5$, where the notation of "0 mol%" means pristine MgH_2

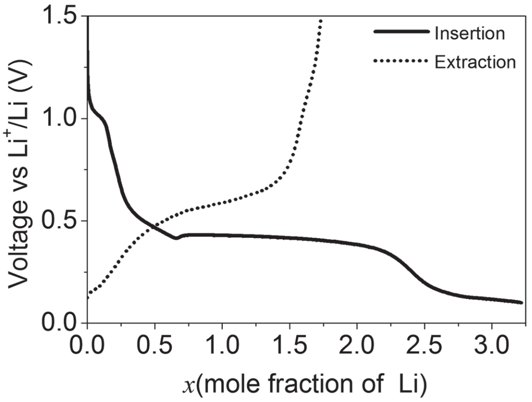

Fig. 2 VC curves corresponding to the Li insertion (solid line) and extraction

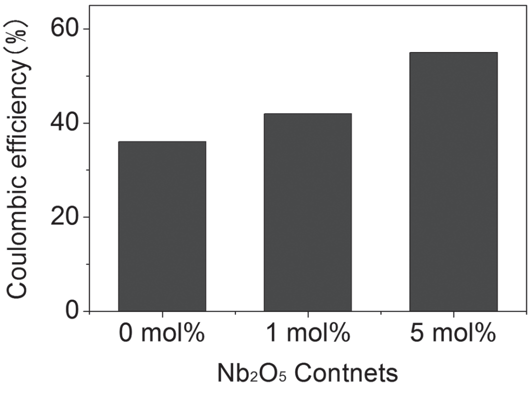

Fig. 3 Coulombic-efficiency of pristine MgH_2 [12], $99MgH_2$-$1Nb_2O_5$ [12], and $95MgH_2$-$5Nb_2O_5$, where the notation of "0 mol%" means pristine MgH_2. In case of $95MgH_2$-$5Nb_2O_5$, mole fraction of extracted Li^+ ions at 2.0 V was estimated by linear extrapolation from the value of it at 1.5 V

values of coulombic-efficiency for pristine MgH_2 and $99MgH_2$-$1Nb_2O_5$ were evaluated from the previous work [12]. Although Li extraction reaction was measured up to 1.5 V from 0.1 V in the case of $95MgH_2$-$5Nb_2O_5$, Li extraction reactions were carried out up to 2.0 V from 0.1 V in the cases of pristine MgH_2 and $95MgH_2$-$5Nb_2O_5$. In order to compare with the previous work, mole fraction of extracted Li^+ ions reaction of $95MgH_2$-$5Nb_2O_5$ at 2.0 V was estimated by linear extrapolation from the value of 53 % at 1.5V. Coulombic-efficiency was increased from 32 % (pristine MgH_2) to 42 % ($99MgH_2$-$1Nb_2O_5$) by adding 1 mol% Nb_2O_5. Moreover, coulombic-efficiency was increased from 42 % ($99MgH_2$-$1Nb_2O_5$) to 55% ($95MgH_2$-$5Nb_2O_5$) by adding further Nb_2O_5. Namely, coulombic-efficiency was increased with increasing Nb_2O_5 contents as follows,

$$Q\ (Nb_2O_5;5mol\%) > Q\ (Nb_2O_5;1mol\%) > Q\ (MgH2) \qquad (4),$$

where, Q (MgH_2), Q (Nb_2O_5;1mol%), Q (Nb_2O_5;5mol%) stand for coulombic-efficiency of pristine MgH_2, $99MgH_2$-$1Nb_2O_5$, $95MgH_2$-$51Nb_2O_5$, respectively.

By taking into consideration that the hydrogen desorption temperature is decreased with increasing Nb_2O_5 contents as formula (3), we could say that coulombic-efficiency is increased as formula (4) with decreasing the hydrogen desorption temperature.

Effect of Nb_2O_5 additive on anode properties of MgH_2 upon the Li extraction reaction was clearer than that upon the Li insertion reaction. On the reaction (1), the right hand reaction proceeds easier than left hand in the first place because ΔG (MgH_2) is larger than ΔG (LiH). In addition, the reaction which produces Mg from MgH_2 through hydrogen desorption is a transition reaction from insulator of MgH_2 to conductor Mg, so this reaction helps electrochemical reaction of the battery. On the other hand, because proceeding of the left hand reaction is difficult, decreasing of activation energy corresponding to hydrogen absorption by adding Nb_2O_5 upon the Li extraction reaction affects coulombic-efficiency to be clearer than decreasing activation energy of hydrogen desorption upon Li insertion reaction.

VC curves corresponding to the Li insertion of pristine MgH_2 (dotted line), $99MgH_2$-$1Nb_2O_5$ (thin line), and $95MgH_2$-$5Nb_2O_5$ (thick line) at a current density of 0.15 mA cm^{-2} and at 100 ℃ are shown in **Fig. 4**. In order to clarify the effect of the additive amount, the current density was chosen to be 3 times larger value than that in Fig. 2. Upon the Li insertion reaction, the voltage curve of pristine MgH_2 shows sudden decrease up to $x = 0.48$, and after that, the voltage curve decrease gradually up to 0.1 V in the range of $x = 0.48$ to $x = 1.97$. In the case of $99MgH_2$-$1Nb_2O_5$, a clear plateau is observed in voltage located at 0.44 V in the range of $x = 0.37$ to $x = 1.4$, and after that, the voltage curve decrease up to 0.1 V. In the case of $95MgH_2$-$5Nb_2O_5$, a clear plateau is also observed in voltage located at 0.4 V in the range of $x = 0.4$ to $x = 1.8$, and after that, the voltage curve is decreased up to 0.1 V like as the voltage curve of $99MgH_2$-$1Nb_2O_5$. Furthermore, the plateau of the $95MgH_2$-$5Nb_2O_5$ had a larger capacity than that of the pristine MgH_2 and $99MgH_2$-$1Nb_2O_5$. Although the VC curve of Li insertion corresponding to $95MgH_2$-$5Nb_2O_5$ shows similar curve of pristine MgH_2 at current density of 0.05 mA cm^{-2} [12], the voltage curve of $95MgH_2$-$5Nb_2O_5$ at current density of 0.15 mA cm^{-2} shows clear and long plateau and it is quite different from that of pristine MgH_2. Namely, effect of Nb_2O_5 additives on anode properties at current density of 0.15 mA cm^{-2} is clearer than that at current density of 0.05 mA cm^{-2}.

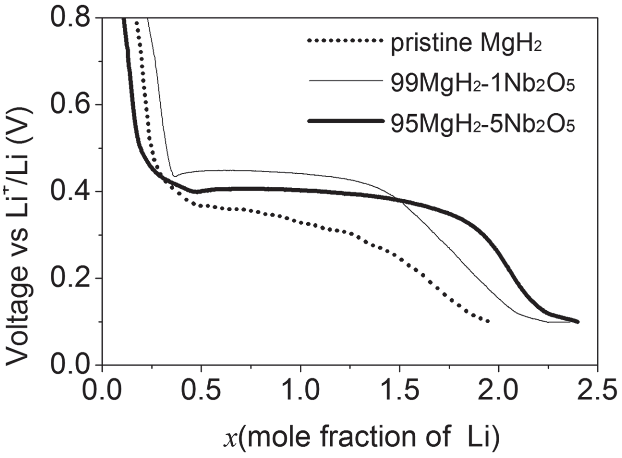

Fig. 4 VC curves corresponding to the Li insertion of pristine MgH_2 (dotted line), $99MgH_2$-$1Nb_2O_5$ (thin line) and $95MgH_2$-$5Nb_2O_5$ (thick line) at a current density of 0.15 mA cm^{-2} and at 100 ℃

Thus, not only coulombic-efficiency but also rate properties are improved by adding Nb_2O_5 with decreasing the hydrogen desorption temperature. This means that electrochemical properties of MgH_2 anode improved by decreasing the hydrogen desorption properties in this system.

4. Conclusions

We fabricated an all-solid-state LIB and investigated anode properties of the catalyzed MgH_2, $95MgH_2$-$5Nb_2O_5$ at 100 ℃ and at current density 0.05 and 0.15 mA cm^{-2}. First, the hydrogen desorption temperature was decreased with increasing Nb_2O_5 contents. Coulombic-efficiency was increased with increasing Nb_2O_5 contents. Namely, coulombic-efficiency was increased with decreasing the hydrogen desorption temperature. Second, rate properties of MgH_2 were improved with increasing Nb_2O_5 contents. Finally, effect of Nb_2O_5 additives on the anode properties is clearer upon the Li extraction reaction than that of Li insertion reaction because of thermodynamical and electrochemical reasons. In addition, upon the Li insertion reaction, effect of Nb_2O_5 additives become clear at 0.15 mA cm^{-2} than at 0.05 mA cm^{-2}.

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