## 論文の要旨

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論 文 題 目

Anode properties of magnesium hydride with all solid state lithium ion batteries

(全固体リチウムイオン電池を用いた水素化マグネシウムの負極特性)

Lithium ion batteries (LIBs) are one of key devices for our current society. LIBs have high energy density and have been utilized for many electric devices, such as cell phone, lap top computer, and electric vehicles in recent years. However, commercial LIBs possess a safety issue due to its flammable liquid electrolyte. An all solid state LIB is composed of nonflammable solid electrolyte and could provide an alternative solution.

Magnesium hydride (MgH<sub>2</sub>) has a potential as an anode material for LIBs and it is one of candidates to satisfy the future market demands. Actually, MgH<sub>2</sub> reacts with lithium (Li) and is transformed into Mg and lithium hydride (LiH), showing large reversible capacity of 1480 mAh g<sup>-1</sup> with an average voltage of 0.5V versus Li<sup>+</sup>/Li by following reaction,

$$MgH_2 + 2Li^+ + 2e^- \leftrightarrow Mg + 2LiH$$
 (1)

On the other hand,  $MgH_2$  is also known as a candidate of hydrogen storage material, because  $MgH_2$  possesses high hydrogen storage capacity of 7.6 mass% and Mg is abundant material. However, in order to derosb hydrogen gas from  $MgH_2$  higher temperature than 300 °C is required due to too slow sorption kinetics to obtain 0.1 MPa hydrogen as an equilibrium pressure. This extremely low reaction speed of hydrogen absorption and desorption has been one of barriers to practical use. Effect of metal oxide additives on hydrogen ab/desorption kinetics of  $MgH_2$  has been examined so far and it is well known that hydrogen ab/desorption kinetics is improved by adding transition metal and metal oxide. Generally, the transition metal oxides (Nb<sub>2</sub>O<sub>5</sub>, Fe<sub>3</sub>O<sub>4</sub>, V<sub>2</sub>O<sub>5</sub>, Mn<sub>2</sub>O<sub>3</sub>, Cr<sub>2</sub>O<sub>3</sub>, and TiO<sub>2</sub>) drastically improve the slow kinetics of MgH<sub>2</sub>. In particular, Nb<sub>2</sub>O<sub>5</sub> is the most effective catalyst to improve the kinetics of the hydrogen ab/desorption reaction among the other metal oxides, such as  $V_2O_5$ ,  $TiO_2$ ,  $Fe_3O_4$ , and so on. Moreover,  $MgH_2$  catalyzed with  $Nb_2O_5$  was rehydrogenated even at room temperature. Whereas,  $Al_2O_3$  and  $SiO_2$  have no clear improvement on the hydrogen desorption reactions.

In this thesis, anode properties of  $MgH_2$  with all solid state lithium ion batteries cell are investigated. In particular, the relationship between the hydrogen desorption properties and electrochemical properties of  $MgH_2$  is focused on to improve battery properties of LIBs. It has been well known that metal oxides improve the hydrogen ab/desorbing properties of  $MgH_2$ . The purpose of this thesis is to clarify the role of additive metal oxide to  $MgH_2$  for all solid state LIBs.

Nb<sub>2</sub>O<sub>5</sub> doped MgH<sub>2</sub>,  $(100-y)MgH_2-yNb_2O_5$  (y=1, 5) and Al<sub>2</sub>O<sub>3</sub> doped MgH<sub>2</sub> (100-z)MgH<sub>2</sub>-zAl<sub>2</sub>O<sub>3</sub> (z=1, 5, 25) were synthesized by ball milling. The insertion and extraction reactions of Li ions from and into the pristine MgH<sub>2</sub> phase of the all solid-state LIB were investigated. Pristine MgH<sub>2</sub> reacts with Li ions electrochemically, producing Mg and LiH even if the experiments were performed with all solid state LIBs as reaction (1).

Coulombic efficiency of the first cycle is 28%, indicating that 72% of the entering Li ions remained in the electrode. Effect of metal oxide (Nb<sub>2</sub>O<sub>5</sub> and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub>) additives on anode properties of MgH<sub>2</sub> was investigates. In the case of Nb<sub>2</sub>O<sub>5</sub> doped MgH<sub>2</sub>, coulombic efficiency of the first cycle was improved from 28% (pristine MgH<sub>2</sub>) to 36% (99MgH<sub>2</sub>-1Nb<sub>2</sub>O<sub>5</sub>) by adding Nb<sub>2</sub>O<sub>5</sub>. Moreover, coulombic efficiency was increased from 36% to 55% with increasing Nb<sub>2</sub>O<sub>5</sub> contents (Nb<sub>2</sub>O<sub>5</sub> contents: 0 mol% to 5 mol%). Effects of the Nb<sub>2</sub>O<sub>5</sub> additive on anode properties at high current or at low temperature were clearer than that at low current density or at high temperature. The hydrogen desorption temperature decreases with increasing Nb<sub>2</sub>O<sub>5</sub> contents, and coulombic efficiency was increased with increasing Nb<sub>2</sub>O<sub>5</sub> contents. Namely, coulombic efficiency was increased with decreasing hydrogen desorption temperature. In the case of  $Al_2O_3$  doped MgH<sub>2</sub>, first coulombic efficiency was improved from 28% (pristine MgH<sub>2</sub>) to 40% (99MgH<sub>2</sub>-1Al<sub>2</sub>O<sub>3</sub>) by adding Al<sub>2</sub>O<sub>3</sub>. Moreover, coulombic efficiency was increased from 28% to 55% with increasing  $Al_2O_3$ contents (Al<sub>2</sub>O<sub>3</sub> contents: 0 mol% to 25 mol%). The hydrogen desorption temperature did not decrease with increasing  $Al_2O_3$  contents. On the other hand, coulombic efficiency was increased with increasing  $Al_2O_3$  contents. Namely, coulombic efficiency was improved by Al<sub>2</sub>O<sub>3</sub>, but hydrogen desorption

temperature did not depend on Al<sub>2</sub>O<sub>3</sub> contents. In order to obtain the local structural information and to clarify that why columbic efficiency was increased by adding Al<sub>2</sub>O<sub>3</sub>, <sup>27</sup>Al-MAS-NMR of Al<sub>2</sub>O<sub>3</sub> doped MgH<sub>2</sub> was carried out. It is known that Al atom in  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> occupied octahedral coordination (AlO<sub>6</sub>) and tetrahedral coordination (AlO<sub>4</sub>). In the case of 75MgH<sub>2</sub>-25Al<sub>2</sub>O<sub>3</sub>, the distribution of AlO<sub>6</sub> was increased and the distribution of AlO<sub>4</sub> was decreased after Li insertion reaction. In addition, peak position of octahedral coordination (AlO<sub>5</sub>) is observed at around 33 ppm. This could act as a binding site for LiH. As a result, the path of hydrogen diffusion between Mg phase and LiH phase is remained, leading to the increasing of coulombic efficiency.

As mentioned above,  $Nb_2O_5$  acts to accelerate hydrogen ad/desortption reactions and  $Al_2O_3$  acts to maintain the path of hydrogen diffusion. Namely, there exist two types of effect of metal oxide additives on anode properties of  $MgH_2$ . One is decreasing activation energy of hydrogen ab/desorption into/from  $Mg/MgH_2$ , which lead to high coulombic efficiency. The other is maintaining hydrogen diffusion path between Mg and LiH, which lead to high coulombic efficiency as well.

Thus "hydrogen" is key and it is important how hydrogen is diffused between Mg and Li. In this thesis, it is clarified that anode properties of  $MgH_2$ is improved by accelerating the hydrogen ab/desorption reactions and maintaining the hydrogen diffusion path in electrode.