

論文の要旨

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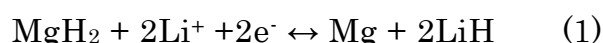
論文題目

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_2) has a potential as an anode material for LIBs and it is one of candidates to satisfy the future market demands. Actually, MgH_2 reacts with lithium (Li) and is transformed into Mg and lithium hydride (LiH), showing large reversible capacity of 1480 mAh g^{-1} with an average voltage of 0.5V versus Li^+/Li by following reaction,



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 desorb hydrogen gas from MgH_2 higher temperature than $300 \text{ }^\circ\text{C}$ 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_2O_5 , Fe_3O_4 , V_2O_5 , Mn_2O_3 , Cr_2O_3 , and TiO_2) drastically improve the slow kinetics of MgH_2 . 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 , 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_2O_5 doped MgH_2 , $(100-y)MgH_2-yNb_2O_5$ ($y=1, 5$) and Al_2O_3 doped MgH_2 $(100-z)MgH_2-zAl_2O_3$ ($z=1, 5, 25$) were synthesized by ball milling. The insertion and extraction reactions of Li ions from and into the pristine MgH_2 phase of the all solid-state LIB were investigated. Pristine MgH_2 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_2O_5 and $\gamma-Al_2O_3$) additives on anode properties of MgH_2 was investigated. In the case of Nb_2O_5 doped MgH_2 , coulombic efficiency of the first cycle was improved from 28% (pristine MgH_2) to 36% ($99MgH_2-1Nb_2O_5$) by adding Nb_2O_5 . Moreover, coulombic efficiency was increased from 36% to 55% with increasing Nb_2O_5 contents (Nb_2O_5 contents: 0 mol% to 5 mol%). Effects of the Nb_2O_5 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_2O_5 contents, and coulombic efficiency was increased with increasing Nb_2O_5 contents. Namely, coulombic efficiency was increased with decreasing hydrogen desorption temperature. In the case of Al_2O_3 doped MgH_2 , first coulombic efficiency was improved from 28% (pristine MgH_2) to 40% ($99MgH_2-1Al_2O_3$) by adding Al_2O_3 . Moreover, coulombic efficiency was increased from 28% to 55% with increasing Al_2O_3 contents (Al_2O_3 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_2O_3 , but hydrogen desorption

temperature did not depend on Al_2O_3 contents. In order to obtain the local structural information and to clarify that why coulombic efficiency was increased by adding Al_2O_3 , ^{27}Al -MAS-NMR of Al_2O_3 doped MgH_2 was carried out. It is known that Al atom in γ - Al_2O_3 occupied octahedral coordination (AlO_6) and tetrahedral coordination (AlO_4). In the case of $75\text{MgH}_2\cdot 25\text{Al}_2\text{O}_3$, the distribution of AlO_6 was increased and the distribution of AlO_4 was decreased after Li insertion reaction. In addition, peak position of octahedral coordination shifts slightly to high magnetic field region and pentahedral coordination (AlO_5) 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/desorption 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.