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学 位 論 文 内 容 の 要 旨

博士の専攻分野の名称 博士（工学） 氏名 張 騰飛

学 位 論 文 題 名

Li-N-H System for Hydrogen Storage: An Investigation on Reaction Mechanism and Catalytic Effect

(リチウム-窒素-水素系水素貯蔵材料の反応機構と触媒効果)

Hydrogen is a kind of independent carrier in comparison to conventional ones, including fossil fuels. It accompanies following advantages such as clean, environmental friendliness and forming water as a non-polluting product during practical applications. Accordingly, reductions of dependence on fossil fuels and emissions of pollutants and greenhouse gases could be realized after using hydrogen as a primary fuel successfully.

Lithium-nitrogen-hydrogen system has been well studied as hydrogen storage materials, since its relatively high capacity of hydrogen and good reversibility during de/hydrogenation. Furthermore, the cost of starting materials is lower than fossil fuels. However, there still have some parts not clearly in this system. Firstly, the reaction mechanism in nano scale between lithium hydride and lithium amide is still need to be investigated in details. To date, little evidence could be acquired from the recent literature showing the position and phase change between each solid phase. Moreover, previous research has shown that some catalysts, especially titanium compounds, have an effect on improving both the hydrogen absorption and desorption kinetics of this system. However, the catalysts which are effective for the de/hydrogenation in the nano scale have not yet been clearly understood. Last but not least, according to the previous approach, from the standpoint of the tuning of small ion mobility, one attempt to enhance the hydrogen-storage properties of the Li-N-H system is to target a catalyst that would effectively increase the mobility of the Li^+ ions.

In the following chapters, these targets will be studied on the basis of a series of experiments. The conclusion will be carefully shown after discussions.

In Chapter 2, it covers the experimental techniques and equipment used during this study, a description of the material and its condition as well as the experimental procedures including details about the sample preparations for each technique. A variety of characterization equipment were used, including a pressure-composition-isotherm (PCI) device, a X-ray diffraction (XRD), two kinds of transmission electron microscope (TEM), a X-ray photoelectron spectroscopy (XPS), a alternating current (AC) impedance, a Thermo-gravimetry (TG), a differential thermal analysis (DTA) equipment and thermal gas desorption mass spectrometry (TDMS).

In Chapter 3, the decomposition mechanism of Li-N-H materials and the catalytic effect of Ti compounds in nano scale were investigated. LiH formed at the surface of LiNH₂ after hydrogenation. During dehydrogenation, LiH particles became smaller since it reacted with LiNH₂ at the interface. Ti compounds, TiCl₃ and LiTi₂O₄, located at the interface between LiH and LiNH₂. The decomposition mechanism and catalysis are believed to be: (a) Li⁺ ion in LiH moved to LiNH₂ through the interface during dehydrogenation. At the same time, H combined and released at the interface; (b) the catalyst of Ti compounds is active in the interface between LiH and LiNH₂. It improves Li⁺ ion migrate among LiH and LiNH₂/Li₂NH using less energy and improve the desorption kinetics.

In Chapter 4, catalytic effects on the dehydrogenation properties of the Li-N-H system with LiTi₂O₄ additive were investigated. The appropriate amount and stability of LiTi₂O₄ on the system were confirmed by the results of TG-DTA-TDMS, XRD and XPS. During dehydrogenation, a storage capacity of 5.7 wt. % was obtained under moderate temperature. A sharp peak of hydrogen desorption occurred at 227 degree C. LiTi₂O₄ is stable after high energy ball-milling and dehydrogenation which is reflected by the XRD patterns and XPS spectrums. The appropriate amount of additive is 0.5 mol % in the sample. The catalytic effect of LiTi₂O₄ probably results from the increasing of the Li⁺ ions mobility between LiH and LiNH₂ solid phases.

In Chapter 5, we have reported the discovery of the relationship between the catalytic effects and the lithium ionic mobility. The conductivity of LiNH₂ and LiH mixtures with catalyst is nearly 1.5 times higher than the sample without catalyst. The catalytic effects of LiTi₂O₄ probably results from enhancing the mobility of the Li⁺ ions between the LiH and LiNH₂ solid phases. We note that the structure characters of LiTi₂O₄ could improve the Li⁺ ionic conductivity which is beneficial to enhance the reaction kinetics. It is hoped that Li-N-H system could be used not only in hydrogen storage but also could be applied in the lithium-ion battery materials.

Chapter 6 is the conclusions of the whole work. Further discussion has been given.