

MODIFICATION OF LIGHT-METAL HYDRIDE
PROPERTIES FOR HYDROGEN-ENERGY
APPLICATIONS

MOHAMMAD BIN ISMAIL

UNIVERSITY OF WOLLONGONG

2011

Modification of Light-Metal Hydride Properties for Hydrogen-Energy Applications

A thesis submitted in fulfilment of the requirements
for the award of the degree

Doctor of Philosophy

from

University of Wollongong

by

Mohammad Ismail

(B.Sc. (Hons) Applied Physics)

Institute for Superconducting and Electronic Materials

November 2011

Declaration

I, Mohammad Ismail, declare that the work presented in this thesis is original and was carried out at the Institute for Superconducting and Electronic Materials, the University of Wollongong, New South Wales, Australia. This thesis is wholly my own work and contains no work previously published or written by another person, unless otherwise acknowledged and referenced. This work is original and has not been submitted to qualify for any other degree elsewhere.

Mohammad Ismail

Acknowledgements

First of all, I would like to express my sincere gratitude to my supervisors, Prof. Shi Xue Dou, Dr. Yue Zhao, and Prof. Yu Xuebin for their intellectual guidance, invaluable support, continual encouragement, and patience throughout this work. Without their help I would never have finished this study.

I also would like to thank the Ministry of Higher Education of Malaysia, for awarding me scholarships to pursue my PhD studies at the University of Wollongong, and my employer, Universiti Malaysia Terengganu (UMT), for granting me study leave and a generous stipend for my family.

I wish to express appreciation for the assistance I received from all the other staff at ISEM, especially Dr. Ivan Nevirkovets, Mr. Darren Attard, Dr Zaiping Guo, Mr. Ron Kinnell, Mr. Rob Morgan, and Miss Crystal Longin for their useful advice and technical assistance. Special thanks also go to Dr. Tania Silver for critical reading of my papers and this thesis.

I also would like to thank my colleagues Dr. A. Ranjbar, Dr. C. K. Poh, J. F. Mao, Lukman Noerochim, and Muhamad Faiz Md Din for all their assistance and support.

My deepest gratitude goes to my beloved parents, especially my lovely mother, and to my brothers, and sisters for their care and support.

Lastly and most importantly, I wish to express my gratitude to my wife, Nurul Hayati Idris, and my daughter, Anis Zahirah. Their patience, encouragement, and understanding enabled me to really concentrate on my study, as was greatly appreciated.

Thank you.

Abstract

Because it is a promising energy carrier, intensive efforts have been made to realize the potential of hydrogen to become a major energy carrier, for both mobile and stationary applications. Solid-state hydrogen storage has become an attractive option due to its high volumetric hydrogen capacity and favorable safety considerations. The purposes of this work are to enhancement the kinetics and tailor the thermodynamics of the light metal hydrides, LiAlH_4 and MgH_2 , using different types of catalyst and the destabilization concept. In this study, a series of single metal hydrides such as NbF_5 -catalyzed LiAlH_4 , SWCNTs-metal-catalyzed LiAlH_4 , TiO_2 nanopowder-catalyzed LiAlH_4 , and HfCl_4 and FeCl_3 -catalyzed MgH_2 ; and a series of combined systems such as MgH_2 - NaAlH_4 and MgH_2 - LiAlH_4 have been systemically investigated for hydrogen storage.

For LiAlH_4 , we found that the hydrogen desorption properties of LiAlH_4 can be improved by doping with NbF_5 . The observed promotion effect of NbF_5 on the dehydrogenation of LiAlH_4 could be explained by combined effect of active Nb-containing species and the function of F anions, which facilitates the dissociation of hydrogen molecules on their surfaces. It was also found that the dehydrogenation temperature and the desorption kinetics of LiAlH_4 were improved by adding with SWCNTs-metal catalyst. The enhancement of the hydrogen desorption properties was likewise due to the combined influence of the SWCNT structure itself, hydrogen spillover effect, and high contact area between carbon and the hydride. All these are responsible for the weakened the Al-H bond, consequently improving the dehydrogenation properties of LiAlH_4 . We have also found that the dehydrogenation properties of LiAlH_4 were improved by doping with TiO_2 nanopowder. The result

shows that TiO_2 nanopowders remain stable during the milling process. The significant improvement is most likely attributable to the TiO_2 nanoparticles act as a surface catalyst, increases the surfaces defects by decreasing crystal grain size in the LiAlH_4 powder, creating a larger surface area for hydrogen to interact, thereby decreasing the temperature for decomposition.

For MgH_2 , it was found that the de/rehydrogenation properties of MgH_2 were significantly improved by mechanically either HfCl_4 or FeCl_3 , and a significant improvement was obtained in the case of the HfCl_4 doped sample. From the x-ray diffraction and x-ray photoelectron spectroscopy results, it appears likely that the significant improvement of MgH_2 sorption properties was due to the catalytic effects of Hf species and Fe that formed during the dehydrogenation process. These species may interact with hydrogen molecules, which may lead to the dissociation of hydrogen molecules and the improvement of the desorption/absorption rate. Besides that, the formation of MgCl_2 may also play a critical role, and there are more likely to be synergetic effects when it is combined with Hf species and Fe.

Another method to improve the hydrogen storage properties of MgH_2 is based on the combined system (destabilization concept). A MgH_2 - NaAlH_4 (4:1) composite system was prepared by mechanical milling to investigate the destabilization effect between MgH_2 and NaAlH_4 . It was found that this composite system showed improved dehydrogenation performance compared with those of as-milled NaAlH_4 and MgH_2 alone. The dehydrogenation process in the MgH_2 - NaAlH_4 composite can be divided into four stages. X-ray diffraction patterns indicate that the second, third, and fourth stages are fully reversible. The formation of NaMgH_3 and $\text{Mg}_{17}\text{Al}_{12}$ phase during the

dehydrogenation process, which alter the dehydrogenation pathway furthermore change the thermodynamic of the reaction play a critical role in the enhancement of dehydrogenation in $\text{MgH}_2\text{-NaAlH}_4$ composite.

We have also systematically investigated the dehydrogenation kinetics and thermodynamics of $\text{MgH}_2\text{-LiAlH}_4$ combined system with and without additives. The improvement of the dehydrogenation properties was likewise attributed to the formation of intermediate compounds, including Al-Mg and Li-Mg, upon dehydrogenation, which change the thermodynamics of the reaction through altering the dehydrogenation pathway. Ten different additives, including TiF_3 , NbF_5 , NiF_2 , CrF_2 , YF_3 , $\text{TiCl}_3 \cdot 1/3(\text{AlCl}_3)$, HfCl_4 , LaCl_3 , CeCl_3 , and NdCl_3 , were added to the $\text{MgH}_2\text{-LiAlH}_4$ (4:1) mixture. Among the additives examined, the titanium-based metal halides, TiF_3 and $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$, exhibited the best improvement in term of reducing the dehydrogenation temperature and enhancing the dehydrogenation rate. It is believed that the formation of Ti-containing and F-containing species during the ball milling or the dehydrogenation process may be actually responsible for the catalytic effects and thus further improve the dehydrogenation of the TiF_3 and $\text{TiCl}_3 \cdot 1/3\text{AlCl}_3$ -added $\text{MgH}_2\text{-LiAlH}_4$ composite system.

Key words: hydrogen storage, lithium aluminum hydride, magnesium hydride, sodium aluminum hydride, catalytic effect, metal halides, single walled carbon nanotube, titanium dioxide, destabilized system