Final Technical Report

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In-Situ Neutron Diffraction Studies of Complex Hydrogen Storage Materials

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The thrust of this project was to investigate the structures of important materials with potential application to hydrogen storage, in an effort to meet the DOE goals for 2010 and 2015, namely 9% (wt) and 15% (wt) respectively. Unfortunately, no material has been found, despite the efforts of many laboratories, including our own, that achieves these goals in a reversible complex hydride such as ammonia borane (NH_4BH_4), and other ammonia based compounds, or with light hydrides such as LiBH_4 , due either to their irreversibility or to the high decomposition temperatures and residual simple hydrides such as LiH from the decomposition of the last named compound.

Nevertheless, several important technical goals have been accomplished that could be valuable to other DOE programs and would be available for collaborative research. These include the development of a high quality glove box with controlled (low) oxygen and water content, which we continue to employ for the synthesis of potential new materials (unfunded research) and the development of a high quality neutron diffraction furnace with controlled gas environment for studies of hydrogen uptake and loss as well as for studies with other gasses. This furnace was initially constructed with an alumina (Al_2O_3) center tube to contain the sample and the flowing gas. The heaters are located in the vacuum space outside the tube and it was found that, for the low temperatures required for the study of hydrogen storage materials, the heat transfer was too poor to allow good control. At temperatures in excess of about 400C (and up to more than 1200C) the heat transfer and control are excellent. For the lower temperatures, however, the center tube was replaced by stainless steel and temperature control to 1C became possible. The paired heaters, above and below the neutron beam window allowed control of the temperature gradient to a similar precision. The high temperature capability of the furnace should make it a very valuable resource for the study of oxides being considered for application to solid oxide fuel cells (SOFCs), in that materials can be studied at potential operating temperatures in both reducing and oxidizing environments to determine their stoichiometry, and lattice parameters.

Our research, which was predicated, in part, on the use of hydrogenous samples (as opposed to deuteration), demonstrated that such studies are feasible and can yield high quality, refinable data. The precision of the refined hydrogen positions appears to be more than adequate for theory calculations (molecular modeling-thermodynamics) and the uncertainty is certainly less than that achieved by attempting to extrapolate the hydrogen positions from refined deuterium positions. In fact the 2008 annual report from the Institut Laue Langevin (ILL), the world's premier neutron scattering laboratory, highlights:

Another trend is the increasing interest in hydrogen. This defies the widespread assumption that neutron diffraction experiments need to be done at deuterated samples. In situ experiments on phase transitions involving hydrogen and in particular on the real time behaviour of hydrogen-storage systems increase in number and scope.

Our work in this area predates the ILL efforts by several years.

Unfortunately, the productivity of our program was significantly curtailed by the unavailability of the MURR powder diffractometer for almost all of the second years of the project. The diffractometer was disassembled to allow partial extraction of the beam tube and replacement of the graphite element that is penetrated by the beam tube. Re-commissioning of the instrument was substantially delayed by errors of the MURR engineering staff, which failed to properly reinstall the sapphire filter that conditions the beam prior to the neutron monochromator, and reduces the radiological background to acceptable levels.

Publications that have appeared based on our studies are listed below. Several other samples are still under investigation and when completed, will be submitted for publication with attribution to the DOE program for financial support.

1. W.J. James, L. Jagat, Q. Cai, W.B. Yelon, J.B. Yang, "Structural Study on Ammonia Borane for Hydrogen Storage", *Materials Science Forum*, **610-613** (2009)425.
2. J.B. Yang, J. Lamsal, Q. Cai, W.B. Yelon, and W.J. James, "Structural evolution of ammonia borane for hydrogen storage", *Appl. Phys. Lett.* **92** (2008) 091916.
3. J.B. Yang, Q. Cai, X.D. Zhou, W.B. Yelon, and W.J. James, "Crystal and electronic structures of novel hydride $\text{Li}_4\text{BN}_2\text{H}_{10}$ ", *J. Appl. Phys.* **102**(3) (2007)033507/1.
4. J.B. Yang, J. Lamsal, Q. Cai, W.B. Yelon, W.J. James, "Study of the crystal structure and phase transition of Li_2NH system", *Materials Research Society Symposium Proceedings* (2008), 1098E(Hydrogen Economy), Paper #: 1098-III103-06
5. J.B. Yang, X. Wang, Q. Cai, W.B. Yelon, and W.J. James, "Crystal and Electronic Structures of Li-N-H and Related Hydrides", *MRS 2006 Fall Meeting Symposium Z Proceedings*, Boston, Nov 27-Dec. 2, 2006.
6. W. B. Yelon, W. J. James, J. Yang, Q. Cai, "In-situ neutron diffraction studies of chemical hydrides," *Preprints of Symposia - American Chemical Society, Division of Fuel Chemistry* **51**(2) (2006)473.
7. J.B. Yang, Q. Cai, X.D. Zhou, W.B. Yelon, W.J. James, and H.U. Anderson, "Crystal and electronic structures of LiNH_2 ", *Appl. Phys. Lett.* **88**(2006) 041914.
8. J.B. Yang, W.J. James, W.B. Yelon, Q. Cai and J. Lamsal, "structural studies of NH_3BH_3 , ND_3BH_3 , NH_3BD_3 and ND_3BD_3 " in preparation