

Hydrogenation of Aluminum by Anodic Coating for AlH₃ Hydrogen Storage Material

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Hydrogen is an effective fuel to overcome the environmental problem. However, hydrogen gas has very small energy per volume and is desired to develop effective way to dense and store hydrogen in a light material. For the purpose of Fuel-Cell Vehicle (FCV), the gravimetric hydrogen content is to be larger than 6 wt%. Aluminum hydride, AlH₃, is promising as a hydrogen storage material due to its large gravimetric and volumetric content (10.1 wt% and 148 kg/m³, respectively) [1]. Despite very low hydrogen solubility and the fact aluminum is one of the most unlikely candidates to form a metal hydride, AlH₃ can be synthesized in even different polymorphic structures by simple organometallic methods [2]. Recently, a new direct-reaction method of synthesizing AlH₃ has been developed under high temperature and pressure [3]. If we succeed in synthesizing AlH₃ or its alloys under moderate condition, AlH₃ will be a hopeful hydrogen storage material. On the other hand, it is a problem that the hydrogenation stops near the interface region between Al and its oxide layers even at high pressure of 10 GPa [3]. We discuss the mechanism by slow diffusion of hydrogen using ab initio molecular dynamics (MD) and propose the effective way to prepare bulk AlH₃ materials by anodic coating.

The α -AlH₃ structure is simulated by ab-initio molecular dynamics method. The ultra soft pseudopotentials with plane wave basis sets are selected. The CASTEP code is used. Figure 1 shows Radial Distribution Functions (RDFs) for α -AlH₃ crystal with experimental lattice constants. At elevated temperatures, H-H and H-Al peaks show broadening. However, the H-hopping are not observed. The hydrogen atoms are located at the interstitial sites during 100 psec of the simulation time. It is also noted that experimentally there are few defects of hydrogen site in α -AlH₃ and the hydrogen atoms do not diffuse [6]. It is found that once α -AlH₃ hydride structure is formed, the AlH₃ structure is stable and it is difficult to diffuse hydrogen.]

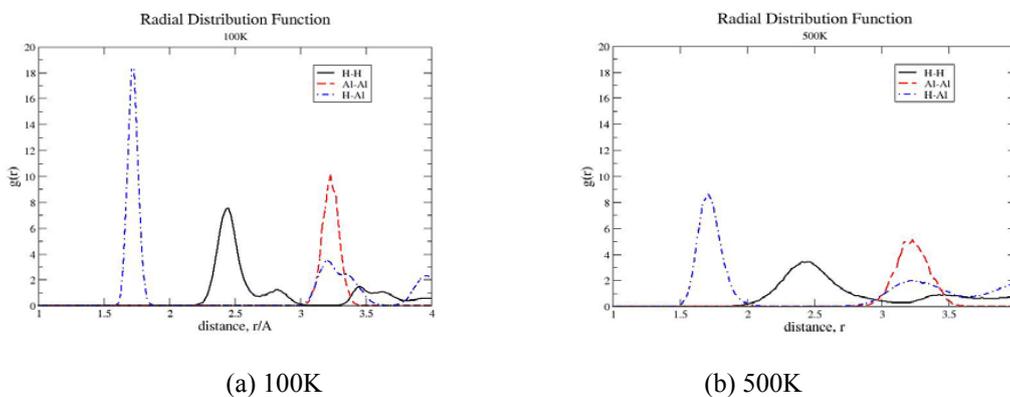


Fig.1 Radial Distribution Functions (RDFs) for α -AlH₃ crystal at (a) 100K and (b) 500K.

This feature can be simulated by phonon calculation. Figure 2 shows the phonon DOS. The structure is experimentally stable at 10 GPa. The simulation also shows the structural stability at 10 GPa. By reducing the pressure, the structure is also stable even at 0 GPa.

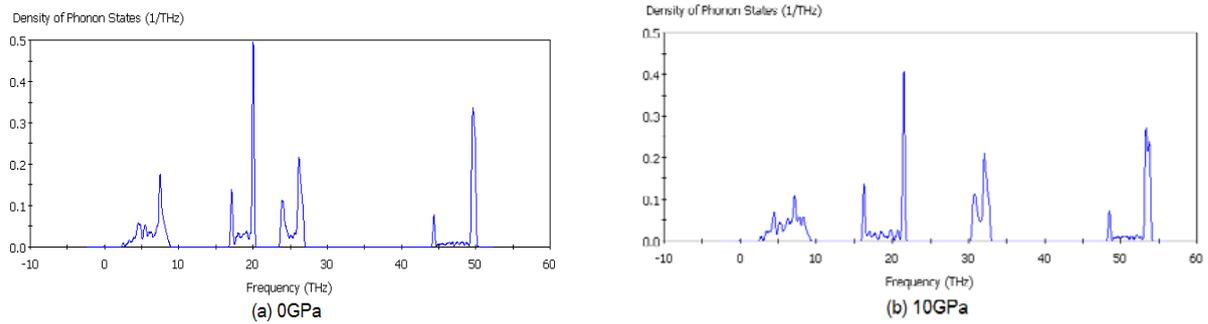


Fig.2 Phonon DOS of α -ALH3 at a pressure of (a) 0GPa and (b) 10GPa.

Figure 3 show the phonon dispersion at 0 GPa. The imaginary eigenvalues do not appear and it shows the α -ALH3 structure is dynamically stable even at 0 GPa.

The hydrogen ordering in Al lattice suppresses the H diffusion and the hydrogenation cannot be developed in whole material.

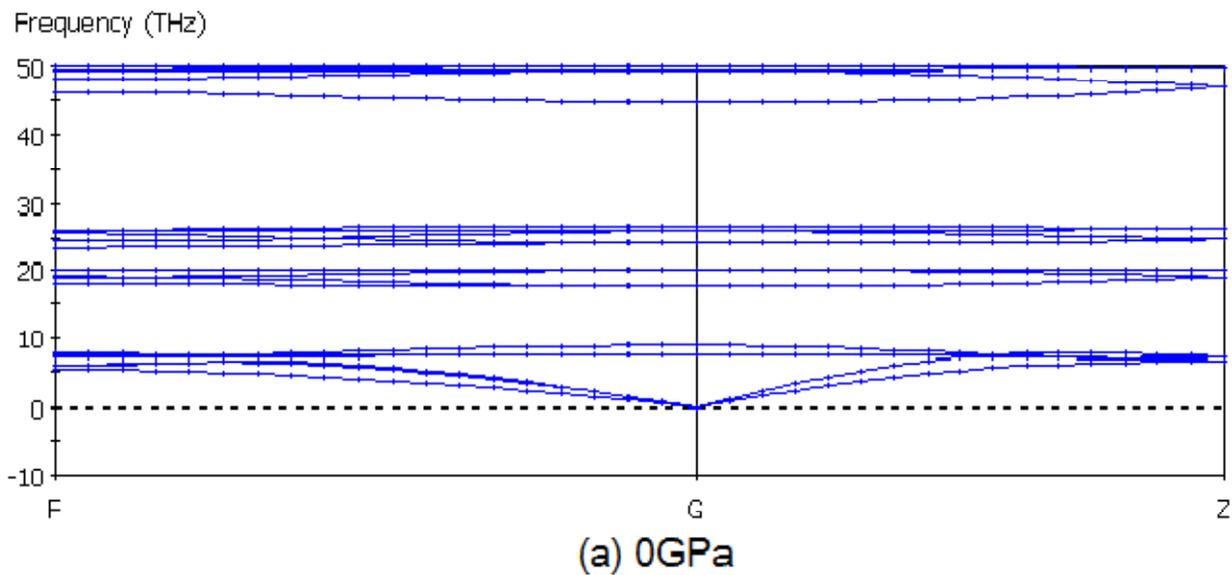


Fig.3 Phonon dispersion of α -ALH3 at 0 GPa.

Our goal is to prepare the hydrogenation of whole Al bulk materials. The key is to facilitate the hydrogen diffusion in Al before generating hydride. Once the hydride is formed near surface of Al, hydrogen does not diffuse into the bulk and hydrogenation stops the surface region. Then it is very important to facilitate hydrogen diffusion into the Al bulk before forming hydride and create the nucleation of hydride far from the surface region. For this purpose, it is necessary to change the bonding of hydrogen in aluminum by some technique. We propose to use anodic coating of Al and change the bonding of H in Al. We hope that the electrostatic field by AlO_x changes the bonding if H in Al and facilitate the hydrogen diffusion.

Figure 4 shows the schematic structure of porous alumina, AlO_x by anodic coating. Nano holes can be seen and the array the holes can be controlled experimentally.

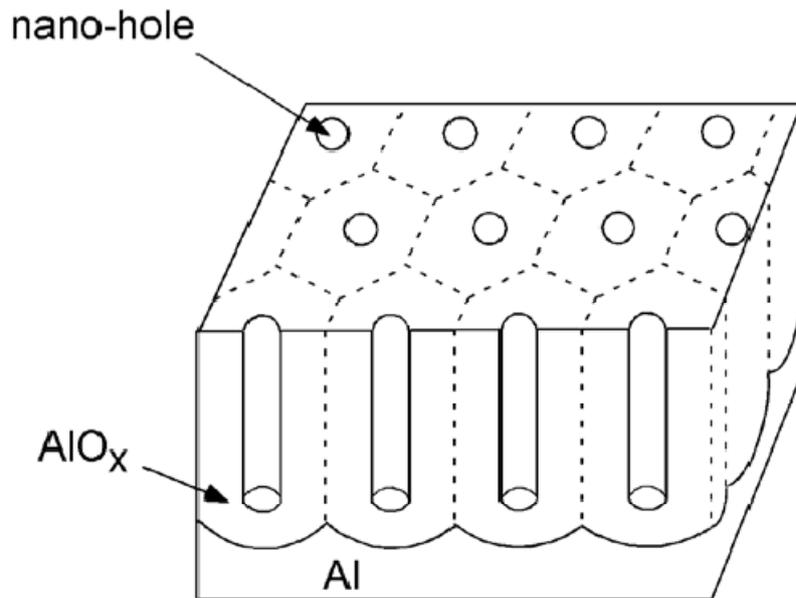


Fig.4 Structure of porous Alumina by anodic coating

Figure 5 shows the SEM image of surface and TEM image of cross section of AlO_x. The beautiful array of nano holes can be seen. We hope the nano holes can be used by hydrogen diffusion path. Usually the oxide layer prohibits the hydrogenation. Therefore, it is necessary to prepare the diffusion path of hydrogen into aluminum.

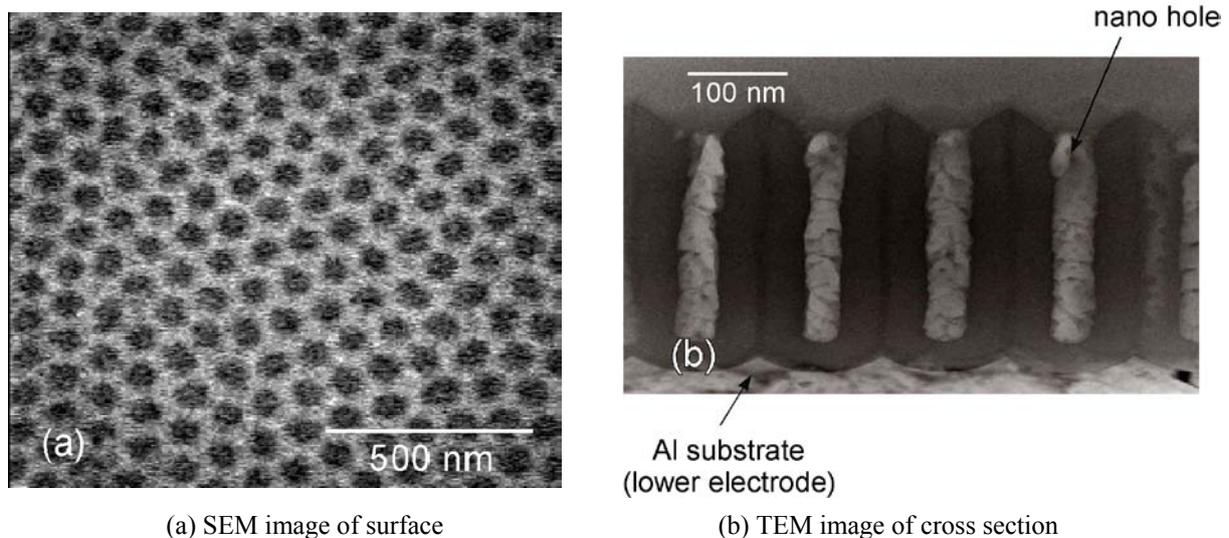


Fig.5 Images of electron microscope. (a) SEM image of surface, (b) TEM image of cross Section

We prepared the samples at NIMS and the experiments of hydrogenation under high pressure at about 9 GPa are performed at Spring8 [6]. The hydrogenation takes place inside the Al bulk by anodic coating. The results will be reported elsewhere. We note that the anodic coating is a hopeful way to prepare bulk AlH₃ materials.

References

- [1] J. Graetz, S., et al., Phys. Rev. B 74 (2006) 214114.
- [2] F. M. Brower, et al., J. Am. Chem. Soc., 98 (1976) 2450.
- [3] H. Saitoh, et al., Appl. Phys. Lett., 93 (2008) 151918.
- [4] V. Tserolas, et al., International Journal of Nanoscience, 8 (2009) 1.

- [5] H. Senoh, et al., *J. Alloys and Compd*, 470, (2009) 360.
- [6] H. Saito at Spring8, private communications (2011).