440f Reversible Hydrogen Storage in Complex Hydrides

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The use of hydrogen as a renewable and clean energy source is one of the most exciting news items to hit this country in a long time. President Bush, during his State of the Union Address in February of 2003, pronounced 1.2 billion dollars to jump-start the Hydrogen Economy. The Hydrogen Economy represents not only freedom from the US dependence on foreign oil, which is a national security issue, but also a necessary step toward improving the environment by eliminating the release of carbon dioxide into the atmosphere due to the burning of fossil fuels. However, hydrogen storage is proving to be one of the most important issues and potentially biggest roadblock, when it comes to implementation of the hydrogen economy. Of the three options that exist for storing hydrogen, i.e., in a solid, liquid or gaseous state, hydrogen storage in a solid is becoming more and more accepted as the only method to have any expectation of meeting the gravimetric and volumetric densities of the recently announced FreedomCar goals; and of all the known hydrogen storage materials, complex hydrides may be the only hope.

Complex hydrides, such as alanates of Na, Li or Mg in particular, are proving to be particularly promising materials because of their very low molecular weight and large fractions of useful hydrogen, which in hydrides is among the highest. For example, $NaAlH_4$ and $LiAlH_4$ theoretically store 5.6 and 8.0 wt% hydrogen, respectively. These values are significantly higher than that of most metal hydrides (0.5–2.0 wt %). However, pure alanates normally show very slow kinetics, with dehydrogenation, for example, taking place at temperatures well above 200°C, and reversibility only being achieved under extreme temperature and pressure conditions. A recent discovery with the complex hydride, $NaAlH_4$, wherein the dehydrogenation and rehydrogenation behaviors were fundamentally changed when this material was doped with a small amount of titanium, initiated renewed and widespread interest in this class of materials for reversible hydrogen storage. So far, the direct consequence of these studies has been the development of a hydrogen storage material containing at least 3 wt% hydrogen that is cyclable at around 110°C. This result is very exciting because for the first time a complex hydride material can be discharged and charged with hydrogen repeatedly over many cycles in a closed vessel, with the behavior mimicking that associated with uptake and release of hydrogen through a simple adsorption-desorption process. Because of this promising result with the Ti-doped $NaAlH_4$ system, research is continuing at a hefty pace with other metal-doped alanates.

The objective of this study is to present the most recent results obtained from the author's laboratory on the dehydrogenation (discharge or desorption) and rehydrogenation (recharge or adsorption) kinetics of $NaAlH_4$, and possibly $LiAlH_4$ when doped or co-doped with Ti and other metals such as Fe and Zr, and different types of carbons such as SWNTs, MWNTs, C60 activated carbon and graphite. To this end, the use of a sonochemical pretreatment step that can be used prior to high energy ball milling to significantly improve the performance of these hydrogen storage materials will also be discussed. The potential reversibility of the Li alanate system through a new physiochemical route will be discussed in light of the conditions that allow it to hydrogenate and hence cycle.