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## Understanding the Role (and Controlling the Behavior) of Transition Metal Dopants in NaAlH<sub>4</sub> Systems

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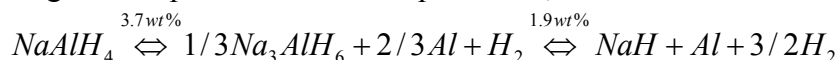
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### Program Scope

Our research program will develop the fundamental materials science and engineering surrounding the behavior of transition metal catalysts added to complex metal hydrides using synchrotron x-ray studies supported by density functional theory and molecular dynamics calculations. The three-year DOE Contract # DE-FG02-05ER46246 was initiated in September of 2005. The overall goals of the research program are to:

- Study correlations between dopant metal (and dopant oxidation state) with hydrogenation/dehydrogenation kinetics;
  - Develop a novel doping scheme using polyelectrolyte layer-by-layer nanotechnology;
- and
- Gain insight into hydride powder surface area variations with high energy milling and also with hydrogenation and dehydrogenation cycling.

Dopant effects and hydrogenation/dehydrogenation behavior of sodium alanate (NaAlH<sub>4</sub>) have been studied extensively making this system well suited to a focused investigation. The work of Bogdanovic and Schwickardi<sup>1</sup> (in 1997) demonstrated reversible hydrogen desorption in the two-step reaction,

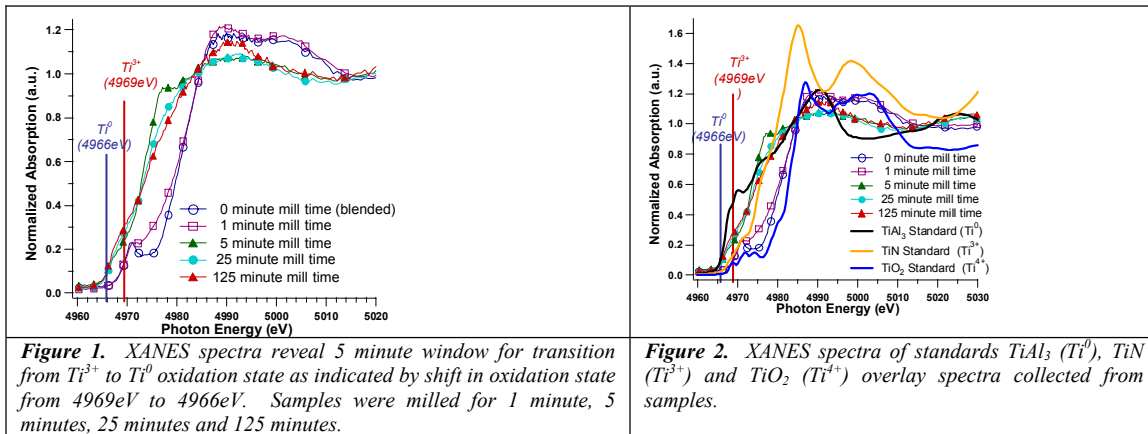


after milling with titanium chloride.<sup>1</sup> In 2003, Anton reported the comparative kinetic enhancements results for various transition metals—and revealed that Ti<sup>2+</sup>, Ti<sup>3+</sup>, and Ti<sup>4+</sup> provide the highest desorption reaction rates.<sup>2</sup> However, a study by Sandrock, et al. shows decrease in reversible hydrogen capacities associated with increasing Ti-dopant content—suggesting detrimental effects associated with excess dopant.<sup>3</sup> In studies which have explored the role of Ti dopants using x-ray absorption spectroscopy at the Ti K-edge<sup>4-10</sup>, it has been realized that an amorphous TiAl<sub>3</sub> phase appears after dehydrogenation and that as-milled systems lead to the formation of nm-Ti or TiAl<sub>3</sub> metallic phases. Aluminum deficiency on the NaAlH<sub>4</sub> lattice (due to TiAl<sub>3</sub> intermetallic formation) is ultimately responsible for controlling hydrogen absorption capacity. The studies supported by this grant will further utilize synchrotron experiments—including small-angle x-ray scattering (SAXS) and x-ray absorption spectroscopy (XAS)—to guide materials engineering solutions related to doping in hydride systems.

## Recent Progress

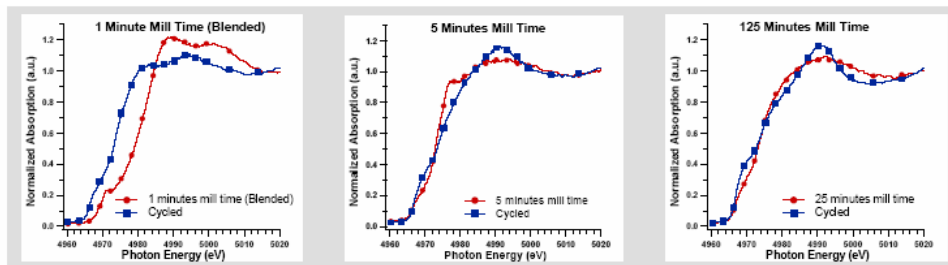
### Effect of Mill Time on Dopant Oxidation State

We examined—by x-ray absorption spectroscopy (XAS)—the Ti K-edge for samples milled for various times (Blended— no milling, 1 minute, 5 minutes, 25 minutes, and 125 minutes). The XAS spectra were comprised of both x-ray absorption near edge structure (XANES) and extended x-ray absorption fine structure (EXAFS) spectra and were collected at the DCM beamline (CAMD, Baton Rouge, LA). The samples contain 2 mol %  $\text{TiCl}_3$  dopant. XANES spectra were collected in the fluorescence detection mode at energies between 4900eV and 5300eV (using 0.3eV stepsize near the absorption edge). XAS spectra were collected between 4770eV and 5970eV (using 1 eV stepsize near the absorption edge). The K-edge for pure  $\text{Ti}^0$  occurs at 4966eV. The absorption energy may shift by (up to 9eV) depending upon the oxidation state of the absorber atom.

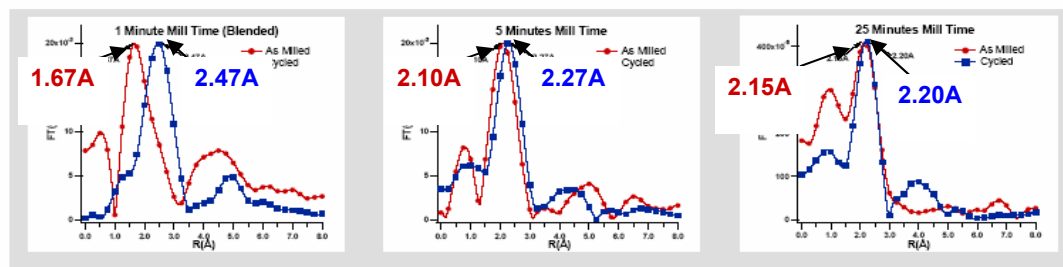


**Figure 1.** XANES spectra reveal 5 minute window for transition from  $\text{Ti}^{3+}$  to  $\text{Ti}^0$  oxidation state as indicated by shift in oxidation state from 4969eV to 4966eV. Samples were milled for 1 minute, 5 minutes, 25 minutes and 125 minutes.

**Figure 2.** XANES spectra of standards  $\text{TiAl}_3$  ( $\text{Ti}^0$ ),  $\text{TiN}$  ( $\text{Ti}^{3+}$ ) and  $\text{TiO}_2$  ( $\text{Ti}^{4+}$ ) overlay spectra collected from samples.



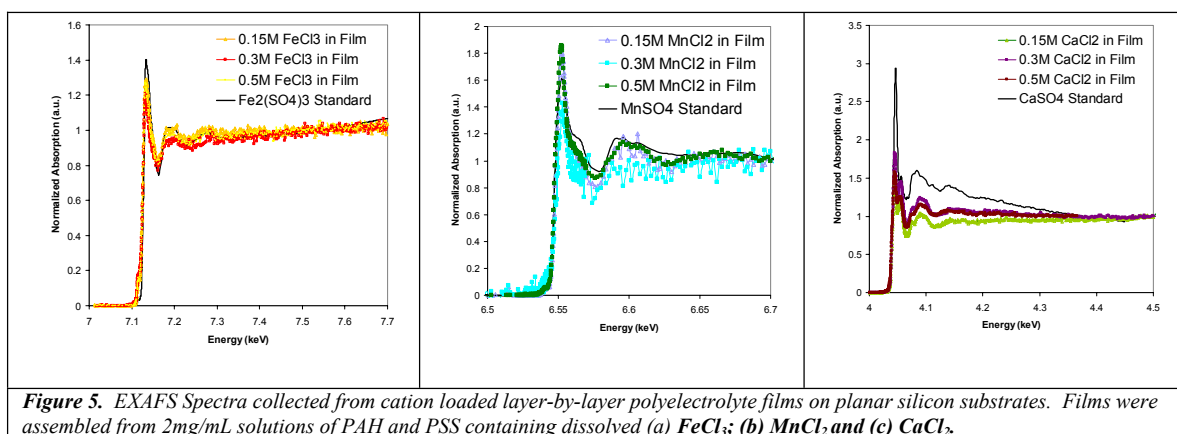
**Figure 3.** XANES spectra before and after a single  $\text{H}_2$  desorption/absorption cycle for samples milled for 1 minute, 5 minutes, and 25 minutes.



**Figure 4.** Fourier Transform of  $\chi(k)$  EXAFS signal for samples milled for 1 minute, 5 minutes, and 25 minutes.—shown here as indicator of distance to first coordination shell around the  $\text{Ti}^{3+}$  or  $\text{Ti}^0$  species. Data are phase shift ( $\delta(k)$ ) corrected and only qualitative trends in these radial distribution functions may be found.

### $M^{x+}$ Cation Loaded Polyelectrolyte assembly onto hydride surfaces.

One approach to mitigate aluminum deficiency would be to decrease catalyst content by directly introducing catalyst at the surface of  $\text{NaAlH}_4$  particles using layer-by-layer self assembly. Because Sandrock, et al.<sup>11</sup> have already demonstrated a decrease in reversible capacities for organic-catalyzed materials in 100-g scaleup  $\text{NaAlH}_4$  powder beds—care must be taken in the selection of polyelectrolytes. The polyelectrolytes selected for these film applications—polystyrene sulfonate (PSS) and polyallylaminehydrochloride (PAH)—are gas/liquid permeable and stable up to  $140^\circ\text{C}$ . These films, formed on planar silicon substrate test pieces, were studied by XAS—revealing that cations (added using precursor  $\text{MCl}_x$ ) are immobilized in the films between sulfonate groups (of PSS). Figure 5 shows XAS spectra of  $M^{x+}$  (where  $M^{x+} = \text{Fe}^{3+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Ca}^{2+}$ ) loaded into polyelectrolyte films. The energy vs. normalized absorption data that  $\text{MCl}_x$  salts undergoes anion exchange from  $\text{Cl}^-$  to  $\text{PSS}^-$  anions—leaving  $M^{x+}$  immobilized in the PSS in film.



**Figure 5.** EXAFS Spectra collected from cation loaded layer-by-layer polyelectrolyte films on planar silicon substrates. Films were assembled from 2mg/mL solutions of PAH and PSS containing dissolved (a)  $\text{FeCl}_3$ ; (b)  $\text{MnCl}_2$  and (c)  $\text{CaCl}_2$ .

### Future Plans

We have used XAS to examine the effect of mill time and our study suggests a 5 minute window of opportunity to control the dopant behavior during milling. We plan to make attempts at tailoring behavior of Ti dopants via...

- Layer by Layer self assembly of films containing dopant cations at the surface of  $\text{NaAlH}_4$  particles and testing of hydrogen desorption/absorption capacities.
- Co-doping (milling with 2 transition metal salts) of  $\text{NaAlH}_4$  particles. Bogdanovic, et al. (2000) report synergistic effect while codoping with Fe and Ti (in 1:1 molar ratio).<sup>12</sup>

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