

IV.B.1d Chemical Hydrogen Storage Research at PNNL

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Objectives

- Quantify borazine release from ammonia borane (AB).
- Develop hydrogen release mechanism for metal amidoboranes.
- Demonstrate high efficiency methods for large-scale synthesis of chemical hydrogen storage materials.
- Develop high-efficiency off-board methods for chemical hydride regeneration to achieve DOE targets (60%):
 - Coordinate with Argonne National Laboratory (ANL) to do preliminary efficiency analysis of regen process.
- Support collaborators through expertise in chemistry and characterization to determine the kinetics and thermodynamics of hydrogen release and regeneration of H-storage materials:
 - Work with Chemical Hydrogen Storage Center of Excellence (CHSCoE) partners to characterize materials and novel approaches to store and release hydrogen.

Technical Barriers

This project addresses the following technical barriers from the Storage section of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) System Weight and Volume

- (B) System Cost
- (C) Efficiency
- (E) Charging/Discharging Rates
- (R) Regeneration Processes
- (S) By-Product/Spent Material Removal

Technical Targets

Scheme 1 represents the focus of materials (ammonium borohydride, ammonia borane, diammoniate of diborane, lithium amidoborane and sodium amidoborane) currently under study and provides both the gravimetric and volumetric density of hydrogen. Table 1 presents a summary of the rates of hydrogen release, enthalpies of hydrogen release and impurities measured for various materials, temperatures and reaction conditions.

SCHEME 1. Materials currently under study and provides both the gravimetric and volumetric density of hydrogen.

Solid phase chemical hydrogen storage materials studied

NH_4BH_4	\Leftrightarrow	$\text{BNH}_x + \text{H}_2$	(240 g H ₂ /kg, 130 g H ₂ /l)
NH_3BH_3	\Leftrightarrow	$\text{BNH}_x + \text{H}_2$	(195 g H ₂ /kg, 140 g H ₂ /l)
$[\text{NH}_3\text{BH}_2\text{NH}_3][\text{BH}_4]$	\Leftrightarrow	$\text{BNH}_x + \text{H}_2$	(195 g H ₂ /kg, 140 g H ₂ /l)
LiNH_2BH_3	\Leftrightarrow	$\text{LiBNH}_x + \text{H}_2$	(109 g H ₂ /kg, 52 g H ₂ /l)
NaNH_2BH_3	\Leftrightarrow	$\text{NaBNH}_x + \text{H}_2$	(76 g H ₂ /kg, 43 g H ₂ /l)

Accomplishments

- Provided high-purity AB to CHSCoE partners and others from our scaled-up first fill reactor.
- Metal amidoborane (MAB) release mechanism identified as metal assisted hydride transfer
- Quantified H₂ impurities from AB and demonstrated approaches to mitigate and control them.
- AB+ metal hydride mixtures showed different features compared to AB: decreased impurities, less foaming, lower exothermic release.
- Demonstrated >99% boron recovery from digestion of real spent fuels.
- Identified potential new AB synthesis route which may be able to combine first-fill and regeneration lowering costs and increasing efficiency.
- Fully characterized spent AB.



TABLE 1. Summary of the rates of hydrogen release, enthalpies of hydrogen release and impurities measured for various materials, temperatures and reaction conditions.

Compound	Gravimetric	Volumetric	Additive	Enthalpy	Peak Rate	Temperature	NH ₃	Bz	Notes	Continue?
	g H ₂ /kg	g H ₂ /l		kJ/mol	g/s/kg	°C	ppm	wt%		C/D
NH ₃ BH ₃	194 (160)	146 (120)	none	-23	1.3	160	100-250	4-12+	foams	D
NH ₃ BH ₃	"	"	none	-23	0.93	145	100-250	2-4	foams	D
NH ₃ BH ₃	"	"	none	-23	0.43	130	100-250	2-4	foams	D
NH ₃ BH ₃ + AF	155 (136)	117 (102)	anti foaming	-23	0.43	130	100-250	2-4	no foam	C
NH ₃ BH ₃	155	117	CoCl ₂	?	?	60	?	0.8	no foam	C
AB:MCM	"	"	scaffold (1:1)	-1 (-22)	2.8	130	100-250	<1	no foam	D
AB:MCM	"	"	scaffold (2:1)	-10	?	130	100-250	<1	no foam	D
AB:MCM	"	"	scaffold (3:1)	-12	1.9	130	100-250	<1	no foam	D
DADB	194 (160)	??	none	-16	1.8	145	?	?	little foam	C
DADB	"		none	-16	0.48	130	?	?	little foam	C
DADB	"		none	-16	0.2	100	?	?	little foam	C
NH ₄ BH ₄	240	130	none	-63	?	40	?	?	little foam	C
LiNH ₂ BH ₃	109	52	none	?	1.76	130	200	0	no foam	D
LiNH ₂ BH ₃	"	"	None	?	0.44	100	2000	0	no foam	D
LiNH ₂ BH ₃	"	"	None	-2	0.08	90	2000	0	no foam	D
LiNH ₂ BH ₃	"	"	None		0.01	80	2000	0	no foam	D
NaNH ₂ BH ₃	76	43	none	?	0.044	80	?	0	no foam	D
NaMeNHBH ₃	30	??	none	?	0.043	100	?	0	no foam	D
KNH(Me)BH ₃	20	?	none	?	?	85	?	0	no foam	D
KNH(^t Bu)BH ₃	15	?	none	?	?	130	?	0	no foam	D

Summary of rates, enthalpies and purity of hydrogen. theoretical density (measured density). Bz = borazine. ? = not yet measured, will be determined in future work. All compositions tested are not shown. C = Continue, D = Discontinue for on or off board transportation systems, still may be applicable for stationary or portable applications

Introduction

Fuel cell vehicles need improved hydrogen storage to meet the DOE driving range targets of 500+ kilometers. To meet this need, the DOE established three Centers of Excellence to develop materials for hydrogen storage. PNNL is part of the CHSCoE which is a partnership between national laboratories, universities and industrial partners. The CHSCoE is tasked with inventing, testing, and recommending chemical hydrides that may meet the DOE targets.

Approach

PNNL's approach is consistent with the philosophy of the CHSCoE. *A comprehensive understanding of reaction mechanisms will enable the development of rational approaches to enhance rates of release, increase purity of hydrogen, and provide energy efficient regeneration schemes.* In addition to a focus on solid state chemical hydrogen storage, PNNL has responsibilities for theory and simulation and core

science and engineering competencies within the CHSCoE. Therefore, PNNL's work within the CHSCoE is inherently multidisciplinary and highly collaborative with several of the CHSCoE partners.

PNNL has many activities including examination of mechanisms of hydrogen release from solid ABs, experimental work on the regeneration of spent ABs, and addressing the materials handling issues associated with solid fuels. PNNL leads the engineering activities within the CHSCoE, which are now targeted toward off-board regeneration of fuels. This group interfaces on a regular basis with DOE's Storage System Analysis Working Group.

Results

Efforts at PNNL in Fiscal Year (FY) 2010 focused on five major tasks: (i) demonstration of scale up of the "first-fill" synthesis of AB, (ii) examining mixtures of AB and metal hydrides, (iii) International Partnership for the Hydrogen Economy (IPHE) materials including

identifying the hydrogen release mechanism from MAB, (iv) quantifying the concentration of impurities, NH_3 and borazine in the hydrogen released from AB, and (v) regeneration.

First-Fill: PNNL demonstrated the bench-scale reactor designed and built in FY 2009. The reactor scaled up PNNL's AB synthesis to 100 g quantities (factor 10x). It is a one-pot synthesis reactor which provides high yield (95-99%) and high purity (>99%) AB. Parametric studies were done using the reactor. The results indicate that a semi-continuous reactor scheme may be viable, and its design is underway. Dow's (formerly Rohm and Haas) analysis of our process indicated that the projected cost was \$9.1/kg AB and the high purity and yield make our process superior to the state-of-the-art.

AB/Metal Hydride Mixtures: We investigated different combinations of AB mixed with metal hydrides (MH), i.e. MgH_2 , CaH_2 , TiH_2 and/or ZrH_2 . We ball milled a series of different combinations of AB+MH powders to obtain tuned materials properties. The composite of ammonia borane+10 mol% TiH_2 shows a remarkable drop in impurity levels to <1%, as compared to neat AB, specifically borazine and ammonia which are released simultaneously with hydrogen. The mixture of AB+0.5 MgH_2 with addition of 10 mol% TiH_2 did not release any detectable amounts of borazine, ammonia or diborane and did not show any foaming. Moreover, the hydrogen release temperature was lowered by ca 20°C.

IPHE Materials and MAB Hydrogen Release

Mechanism: A new series of substituted metal amidoboranes MNRBH_3 ($\text{M} = \text{Li, Na, K}$; $\text{R} = \text{H, CH}_3^-$, $\text{C}(\text{CH}_3)_3^-$) have been synthesized. A detailed study has indicated that hydrogen release takes place through a metal ion-assisted hydride transfer mechanism and the formation of a metal hydride intermediate. In these compounds the dihydrogen bonding of the parent AB has been replaced by a $\text{M}^+ \dots \text{H}^\delta \text{B}$ interaction and this, in agreement with our detailed studies of release from AB, may explain why there is no induction period observed. No ammonia (<10 ppm) was observed for the materials when the material is decomposed in a sealed reactor and the strong dependence of reaction rate on temperature suggests the materials will be unaffected by storage at even high ambient temperatures.

The reactivity trend of hydrogen release from metal amidoboranes is the opposite of the reactivity trend of hydrogen release from metal borohydrides. In the case of the MABs the metal cation performs a hydride transfer (or relay) from the neighboring borane to the protonic hydrogen of the amine. This is interesting from a mechanistic outlook as the formation of the nascent metal hydride is faster for the more stable hydrides, however the more stable the metal hydride the greater the barrier for hydride transfer to the amine – thus the rates for each step are opposite in reactivity the observed

rates tend to be moderated. However, as the $\text{K} > \text{Na} > \text{Li}$ the formation of the nascent MH appears to be rate limiting and therefore give the opposite reactivity of the corresponding borohydrides, that is $\text{Li} > \text{Na} > \text{K}$. As the ionization energy increases, the activation barrier for the M-step decreases, whereas the activation barrier for the H-step increases thereby explaining why the rate trend for release is $\text{K} > \text{Na} > \text{Li}$ [1].

Impurities from AB: Hydrogen generated from AB decomposition was analyzed using various analysis tools such as nuclear magnetic resonance (NMR), Fourier transform infrared, and mass spectrometry to determine the ammonia and borazine levels. Quantitative amounts of borazine was found by bubbling AB-generated hydrogen with a sweep gas of 20 ccm nitrogen through a liquid trap (Tetrahydrofuran or glyme) which captured the borazine impurities. We then used solution NMR to measure the amount of borazine produced. Figure 1 contains a summary of the results. It was determined that the ramp rate and temperature impacted the amount of borazine produced, with the temperature being the dominant factor. At temperatures below 150°C, the borazine levels was <1 wt%, but increased by an order of magnitude when the temperature exceeded 150°C. High temperatures combined with fast temperature ramping (>5°C/min) increased the borazine levels to >12 wt%. As far as we can tell the ammonia produced (100-250 ppm) was independent of temperature and ramp rate within our experimental error of measuring ammonia with a Draiger tube. In addition, if the reactor was sealed during hydrogen generation, and the hydrogen released slowly much less ammonia was detected indicating that residence time impacted the ammonia production rate. This is especially true for the MABs. Additives impacted the impurities in different ways. For example, both AB on mesoporous silica scaffolds (1:1) and AB mixed with CoCl_2 (<5 wt%) were found to have decreased borazine (<1 wt%) produced even at temperatures >150°C and ramp rates >5°C/min; however, AB on a BN scaffolds resulted in no improvements in regards to borazine

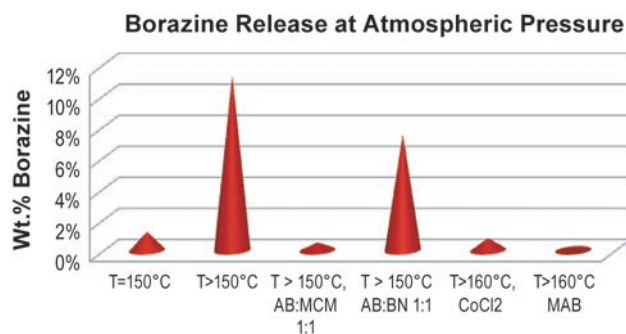


FIGURE 1. Summary of Borazine Release from AB and AB with Additives

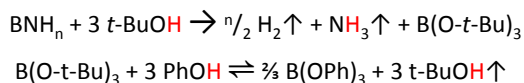
production. Since high temperature and ramp rates will be required to generate hydrogen in sufficient quantity to meet the hydrogen generation targets, neat AB research should be discontinued. However, AB with additives such as CoCl_2 showed low borazine release, and CoCl_2 significantly reduced foaming making AB with additives a “Go” decision for future research. Metal amidoboranes did not produce any borazine since the release mechanism is different than that of AB; however, the ammonia release was higher (0.2 wt%) than that of AB.

Regeneration of Spent Fuel: Another key aspect of the PNNL project is chemical regeneration. A process then was envisioned as shown in Scheme 2; where R is an alcohol such as *tert.*-butanol; PhOH is phenol; M is a transition metal complex. PNNL has found precedent for and demonstrated all the steps individually.

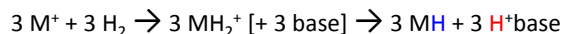
Digestion chemistry had been demonstrated using model spent fuels in previous years: borazine and borazine-derived polyborazylene. However, information is needed to assess regeneration cost and efficiency of real spent fuel. In FY 2010 we worked on digestion of real spent fuels obtained from AB dehydrogenation. Monothiol do not digest spent fuel. We tried to transesterify alkyl borates with thiophenol, but those reactions were unsuccessful. Digestions with aliphatic alcohols produce borate esters and a white residue, to varying degree depending on the alcohol. We optimized reaction conditions to maximize total conversion and recovery of boron. Approximately 85% of the boron was recovered as $\text{B}(\text{OEt})_3$. This ester as well as other alkyl borates can be transesterified with phenols to produce aryl borates [2]. The boron residue was recovered as boric acid by adding aqueous HCl. Boric acid converts to $\text{B}(\text{OAr})_3$ under same conditions as used for transesterification [2]. Therefore it is envisioned that >99% B can be recovered. Digestion with ammonium

SCHEME 2. Process using Transition Metals Catalysts to Regenerate Spent AB Fuel

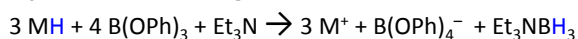
1) Digestion



2) Transition Metal Hydride Formation



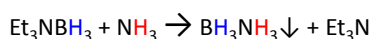
3) Hydride Transfer/Ligand Redistribution



4) Recycle



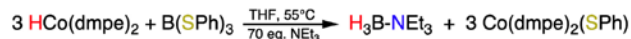
5) Ammoniation



tetrafluoroborate was tried since we have been able use BF_3 in reactions analogous to Step 3 using $\text{HRh}(\text{dmpe})_2$. Reacting NH_4BF_4 with spent fuel in effect combines Steps 1 and 4 to accomplish recycling of BF_4^- byproduct of Reaction 3.

All the steps of Scheme 2 have been demonstrated using Rh based catalysts. Due to the high cost of Rh, lower cost transition metals (Co and Ni) were examined. In FY 2009 PNNL synthesized complexes with dmpe and other bis phosphine ligands and explored their properties and reactivities (for steps 2 and 3). The results show that $\text{HCo}(\text{dmpe})_2$ is not strong enough of a hydride donor to transfer a hydride to $\text{B}(\text{OPh})_3$. However, it readily transfers H^- to $\text{B}(\text{OC}_6\text{F}_5)_3$, which has greater H^- affinity compared to $\text{B}(\text{OPh})_3$. On the basis of these observations and recent theoretical analyses, PNNL in FY 2010 examined the use of chlorophenols and fluorophenols in place of phenol in the above process with complexes of Co and Ni. We used theory to identify aromatic borate esters with hydride affinities greater than that of $\text{B}(\text{OPh})_3$. Literature reports [3] suggested that halogenated phenyl borates would have greater Lewis acidity than phenyl borate. We calculated hydride affinities for several chloro and fluoro-substituted phenyl borates and found indeed that hydride affinities could be significantly increased by halogen substitutions. In collaboration with US Borax scientists (Dave Schubert and Duane Wilson), several compounds were synthesized and characterized by NMR. Their relative Lewis acidities were determined as well based on the adduct with triethylphosphine oxide. We used this index to corroborate calculated hydride affinities and correlate with reactivity toward $\text{HRh}(\text{dmpe})_2$ and $\text{HCo}(\text{dmpe})_2$ and identified the most likely halogenated phenyl borates for Step 3. We found that Co hydrides de-chlorinate chlorophenyl borates. The reactions of $\text{HCo}(\text{dmpe})_2$ with less than fully fluorinated phenyl borates are complex. Evidence for hydride transfer to 2-fluorophenyl borate was not observed, suggesting that esters of mono-fluorophenols do not have high enough hydride affinity. $\text{HCo}(\text{dmpe})_2$ did react with the borate ester of 3,5-difluorophenol and evidence of hydride transfer was observed, but the reaction was complicated by side reactions that consumed B-H containing products and partially decomposed the $\text{Co}(\text{dmpe})_2^+$ complex.

Reactions of $\text{B}(\text{SPh})_3$ with $\text{HCo}(\text{dmpe})_2$ and $\text{HNi}(\text{dmpe})_2^+$ were investigated to assess the range of boron compounds that could be reduced with these hydrides. For the Co complex, facile reduction of all B-S bonds to B-H bonds occurs. Reactions run in the presence of triethylamine produced triethylamine borane as the sole boron containing product.



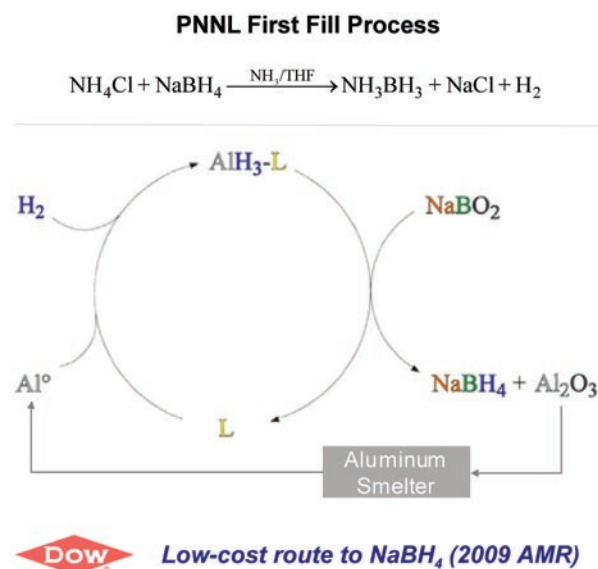
For the Ni complex, two of the three B-S bonds were readily replaced to give $\text{PhSBH}_2\text{NEt}_3$. As mentioned, digestion of spent fuel to $\text{B}(\text{SPh})_3$ has not been demonstrated. Also, these reactions produce metal complexes with SPh ligated to the metal. Digestion to $\text{B}(\text{SPh})_3$ and recycle of these complexes remain to be worked out.

Finally, Dow's cost analysis of AB synthesis revealed the most significant cost being NaBH_4 production from $\text{AlH}_3\text{-L}$ (Scheme 3). Adding to the cost is the fact that 25% of the hydrogen in the NaBH_4 is lost in the conversion to AB. After looking at the process production route, we believe that AB could be produced directly from the $\text{AlH}_3\text{-L}$ improving the hydrogen utilization and eliminating NaCl production potentially resulting lower cost (Scheme 4). A literature search revealed that all the steps of PNNL's proposed process have been demonstrated except one. We successfully demonstrated that step this year. This process still requires Al° , which is very expensive to produce. We believe there is a way to avoid the smelting process and potentially decrease the cost of AB synthesis. If the smelting process can be avoided, then this new synthesis process would also be applicable to regeneration of spent fuel. Therefore, a single facility could be used for fuel synthesis and spent fuel regeneration decreasing capital costs. This is a recommendation for future work.

Conclusions and Future Directions

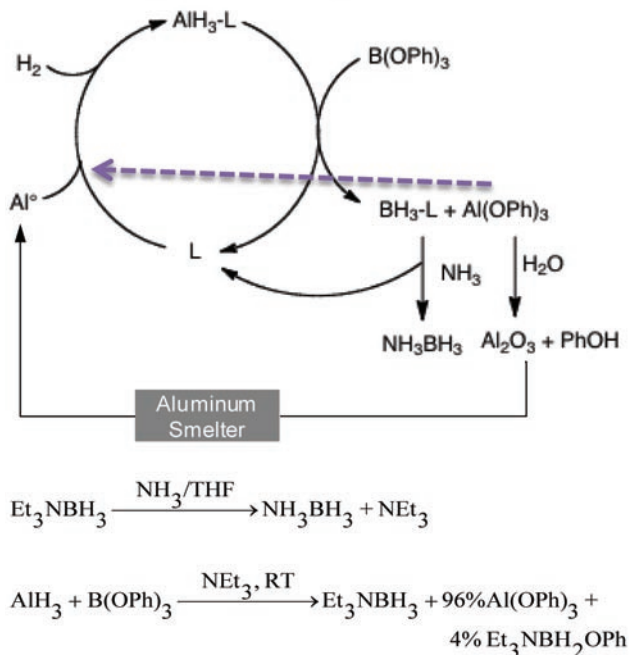
Conclusions

- Bench-top scale AB synthesis reactor demonstrated a 10x increase in AB production capability showing



SCHEME 3. PNNL First-Fill AB Synthesis Route

Proposed Direct Synthesis Scheme



SCHEME 4. Proposed new direct AB synthesis route. The two reactions shown are key reactions demonstrated by PNNL to make the route possible, one was demonstrated in FY 2009 the other this year. The dotted line shows the proposed route to avoid the aluminum smelting process.

that the PNNL process can be successfully scaled-up. In addition, parametric studies with the batch reactor enable the design of a semi-continuous reactor.

- AB + metal hydride mixtures showed different features compared to AB, with some mixtures showing no borazine production, less foaming, and lower exothermicity.
- Quantified impurities in H_2 from AB and demonstrated approaches to mitigate and control.
- In order to meet the hydrogen generation targets, the ramp rate and temperature needed for AB to generate hydrogen also result in high impurities, it is recommended that neat AB not be further developed for use in on-board hydrogen storage.
- AB with additives such as CoCl_2 can meet the hydrogen generation rates without producing excessively large amounts of borazine, further development of AB with additives is recommended.
- Identified potential new AB synthesis/regeneration route.
- Since the chlorinated phenyl borates undergo dechlorination in reactions with Co hydrides, work to develop AB regeneration via this system is not recommended.

Future Work

This project has ended. Therefore the future work is primarily working with the Engineering Center in the development of systems. Recommendations for future work based on this project include:

- Development of a flow reactor for AB synthesis.
- AB with additives to reduce borazine impurities.
- Investigation of the new AB synthesis/regeneration route.
- Metal amidoborane development to find an endothermic system that is regenerable on-board.
- Develop and assess routes for converting spent fuel to B(SPh)₃ and recycle of Co(dmpe)₂SPh and [Ni(dmpe)₂SPh]⁺.
- Develop better understanding of reactions of fluorinated phenyl borates with Co hydrides to assess feasibility of their use in regeneration scheme.
- Assess reactivity of fluorinated and chlorinated phenyl borates using Ni⁺ hydrides.

FY 2010 Publications/Presentations

Publications

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12. E Ronnebro, High-pressure techniques for discovering and rehydrogenation of metal hydride materials, *J. Physics and Chemistry of Solids*, in press **2010**.
13. RS Chellappa, M Somayazulu, VV Struzhkin, T Autrey, RJ Hemley. Pressure-induced complexation of NH₃BH₃-H₂. **2010** Submitted to *J. Chem. Phys.*
14. RS Chellappa, T Autrey, M Somayazulu, VV Struzhkin, RJ Hemley. High-pressure hydrogen interactions with polyaminoborane and polyiminoborane. *Chemphyschem.* **2010**. 11(1):93.
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Presentations

1. JD Holladay, National Hydrogen Association, Long Beach, CA (May 2010).
2. E Ronnebro, 4th Symposium on Hydrogen & Energy, Wildhaus Switzerland (Jan 2010).
3. AJ Karkamkar, American Chemical Society, Boston MA (Aug 2010).
4. TD Smurthwaite, American Chemical Society Joint Northwest/ Rocky Mountain Meeting, Pullman WA, (June 2010).
5. JD Holladay, Materials Challenges in Alternative & Renewable Energy 2010, Cocoa Beach FL (Feb 2010).

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