HYDROGEN STORAGE IN POLYMER-DISPERSED METAL HYDRIDES (PDMH)

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Abstract

Metal hydrides, dispersed in a polymeric matrix, are under investigation as unique hydrogen storage media. It is proposed that the relatively low gravimetric capacity of metal hydrides can be significantly enhanced by incorporating a low-density polymer that can both interact with the hydride on a molecular level, and store additional hydrogen within the polymer structure. An extensive series of polymers, varying in chemical structure, composition and thermal stability, were processed thermally, mechanically or by plasma spray techniques and evaluated for hydrogen storage capacity. Select combinations of polymer and processing method are undergoing further evaluation for hydrogen storage capacity when combined with specific metal hydrides. In this manner, the experimental design space of polymer/process/metal hydride can be explored to better understand the benefits provided by polymer-dispersed metal hydrides (PDMH). In addition to conventional pressure composition isotherm (PCI) measurements, PDMH samples are characterized by thermal analysis, electron microscopy and electron paramagnetic resonance techniques. The last method is particularly important for probing the creation of free radicals that may result from processing the polymers. It is likely that free radicals play a critical role in the mechanisms of hydrogen storage in PDMH – possibly facilitating hydrogen dissociation and enhancing molecular interactions with the metal hydride.

Introduction

Hydrogen storage has been extensively studied in recent history and yet no single technology currently meets automotive goals of 5.5 wt% gravimetric capacity and 60 kg/m^3 volumetric capacity. Although many hydrogen storage methods are under consideration, including, but not limited to, carbon nanotubes, liquid hydrogen, compressed gas, and metal hydrides, United Technologies Research Center has focused on a novel approach by dispersing metal hydrides in polymer support phases. The primary advantages of metal hydrides are the relatively high volumetric capacity and the inherent safety of such systems – applied heat is required to release hydrogen. The intent of this contract activity is to explore the preparation of 'Polymer Dispersed Metal Hydrides,' or PDMH, and assess their value as a unique storage medium for hydrogen. The goal is to advantageously combine the volumetric storage capacity of metal hydrides, with the low density of polymeric materials, in an effort to improve the gravimetric storage capacity by factors of 2-5 relative to non-dispersed metal hydrides. In addition, it is conceivable that dehydriding temperatures may be reduced, potentially enabling automotive waste heat to effectively dissociate the hydride. Dispersion of the metal hydride in a polymer support phase may also increase the stability of the metal hydride, possibly through reduction of hydride decrepitation (Meinzer 1994).

Prior to this effort, little experimental data existed on the hydrogen storage capacity of PDMH systems, although arguments were made supporting the expected increase in PDMH gravimetric capacity over the metal hydride alone, based solely on relative density (Jarvi 1999; Meinzer 1994). Preliminary work at UTRC measured hydrogen weight loss, as a function of temperature, for several metal hydrides and polymers containing these metal hydrides. Figure 1 summarizes these data. Comparing results for TiH_2 alone, and Polymer 3 plus 5% TiH_2, the data indicate that the combination of TiH_2 and Polymer 3 provides a factor of 15 increase in the weight of hydrogen released, at constant temperature. Specifically, this sample was a plasma-sprayed blend of Kapton polyimide and TiH_2. By extending this 15X performance increase to magnesium hydride or other high capacity hydrides, it was envisioned that the DOE goal of 5.5 wt% gravimetric capacity could be readily achieved. Moreover, the successful demonstration of such high storage capacity could lead to an economical weight/volume ratio for a fuel tank sized for current gasoline fueled automobiles (DeLuchi 1992; Dillon, *et al*. 1997).

Unfortunately, metal hydrides exhibiting higher gravimetric capacities also tend to exhibit poor dehydriding kinetics and generally require higher temperatures to access the maximum amount of hydrogen (e.g. MgH_2). Table 1 provides a list of metal hydrides and corresponding properties as adopted from http://hydpark.ca.sandia.gov/. Temperature limitations must be considered carefully during the selection and processing of metal hydrides within a polymer support matrix. Nevertheless, hydrogen storage in metal hydrides remains an active area of research because of their potential use as simple, compact, robust and potentially inexpensive storage devices.

The prime objective of UTRC's innovative research program in PDMH is to characterize the performance and mechanism(s) of hydrogen storage in these materials, while pursuing DOE goals. Initial efforts focused on determining the hydrogen storage capacities of the polymers separately from those of the well-established metal hydrides. PDHM samples demonstrating suitable performance enhancement over baseline metal hydrides would be prepared in larger

quantities to examine scale-up effects. Based on the optimum performance obtained in this program, a brief system assessment would be performed in view of the DOE capacity goals. The assessment would provide preliminary cost estimates for a hydrogen storage bed and an analysis of the thermal requirements for hydrogen delivery, for an appropriately sized system.

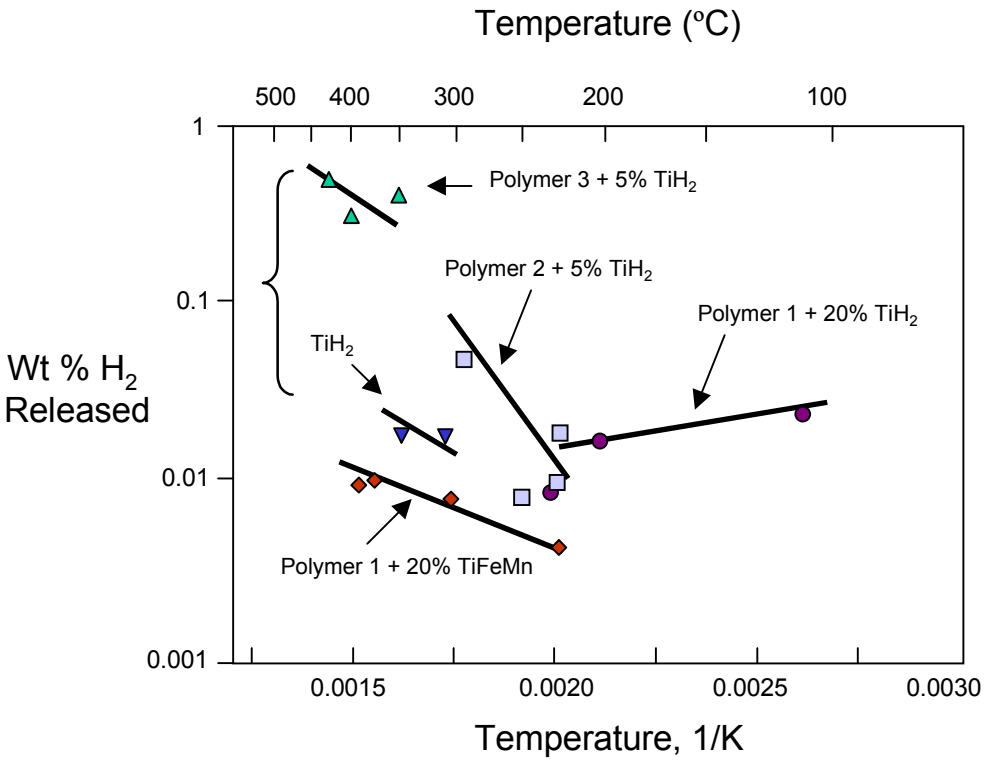

Figure 1. Early UTRC Measurements of Hydrogen Released from Various PDMH

Table 1. Representative Metal Hydrides Considered in this Study

Material Selection - Metal Hydrides

Metal Hydride	T(C@1atm)	wt.% H_2 stored	commercial source
$Ti(Fe_{0.9}Mn_{0.1})$	3	1.90	Ergenics Hy-Stor 102
$LaNi_5$	12	1.49	Ergenics Hy-Stor 205
$CaNi_5$	43	1.87	Ergenics Hy-Stor 201
$LaNi_{4.7}Al_{0.3}$	45	1.44	Ergenics Hy-Stor 207
$Ti(Fe_{0.8}Ni_{0.2})$	73	1.30	Ergenics Hy-Stor 103
Mg_2Ni	255	3.60	Ergenics Hy-Stor 301
Mg	279	7.66	
Ti	643	3.98	

Experimental Methods

The general experimental approach for this study is shown pictorially in Figure 2. The approach is designed to probe polymer/processing method/metal hydride design space, but initially focuses on the effect of processing on polymer structure. In this manner, the hydrogen storage capacity of the polymer phase can be independently examined from that of the metal hydride in a PDMH.

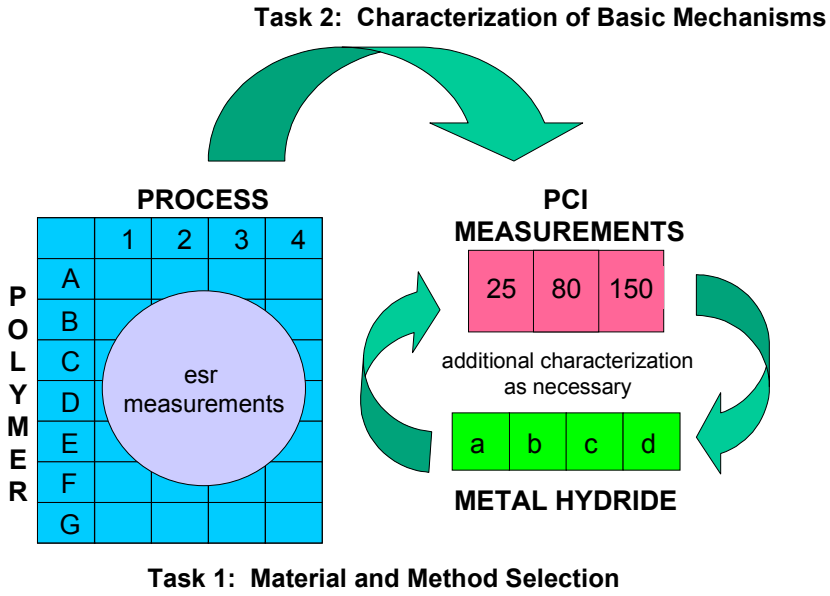

Figure 2. Experimental Approach for PDMH, Showing Relationship of Tasks

Generically speaking, polymers (A-G) undergo various processing methods (1-4) and are characterized following sample preparation. One method to characterize structural changes of polymers is electron spin resonance (ESR) or electron paramagnetic resonance (EPR) spectroscopy, in which microwave radiation induces transitions between magnetic energy levels of electrons with unpaired spins. Unpaired electrons are relatively unusual in occurrence, but are present in free radicals, triplet electronic states and transition metal ions. Unpaired electrons of free radicals are generally left following homolytic fission of a covalent bond – *i.e.* polymer chain scission (Willard, *et al*. 1981). Thus, EPR provides a means to probe the concentration of free radicals in a polymer sample.

Polymers were selected to cover a wide range of chemistries and level of thermal stability. All polymers were obtained as samples or purchased from commercial vendors and used as-received. Nafion NR-50 superacid catalyst was obtained from Engelhard (Seneca, SC). Polyaniline powder was purchased from Ormecon Chemie (Ammersbek, Germany). Polytetrafluoroethylene (PTFE), polyamide (Nylon 6), polyetheretherketone (PEEK) and polypropylene (PP) powders were purchased from Goodfellow (Berwyn, PA). Polyvinylidene (PVDF) powder was purchased from Aldrich (Milwaukee, WI). A very limited quantity of ground Kapton polyimide was obtained from DuPont (Wilmington, DE) – a surrogate polyimide, LaRC-SI, was obtained from Imitec, Inc. (Schenectady, NY).

Polymer samples were processed using four methods - no additional processing (as-received), thermally, mechanically, or by plasma spray. The relative thermal stability of each polymer was studied using thermogravimetric analysis (TGA). These experiments were performed using a TA Instruments TGA 2950 (New Castle, DE), in both argon and air, with a heating rate of 5ºC per minute from room temperature to 800ºC. Based on the TGA results, bulk portions of each polymer were subjected to thermal processing in flowing argon to 80ºC, 150ºC or 400ºC in a conventional tube furnace. Additional portions of polymer samples were mechanically milled for 0.5 or 2 hours in an 8000D SPEX CertiPrep Dual Mixer/Mill® (Metuchen, NJ) with hardened steel vials and steel balls. Polymer samples were arc plasma-sprayed at ZatorskiCo (East Hampton, CT) using parameters suitable for delivering powder-based coatings of engineered plastics. Most powders were sprayed using a standard Metco 3MB plasma spray gun, a GP or GH nozzle, a customized Sultzer-Metco Twin 10C powder feeder, primary gas flow rates of 150 SCFH, an applied voltage of 60V and a current of approximately 300A. The spray gun was mounted in a custom capture vessel, which reduced the velocity of the expanding gas through expanding cross-section, allowed convenient capture of the sprayed powder, and provided for gas venting.

The hydrogen storage capacity of each processed polymer sample was measured. Hydrogen absorption/desorption measurements were performed at Advanced Materials Corporation (Pittsburgh, PA) and UTRC using a computer-controlled, gas reaction controller pressure-composition isotherm (PCI) measurement system from Advanced Materials Corporation. The PCI unit was equipped to operate over a pressure range of 0.01 to 50 atmospheres of hydrogen and a temperature range of 25ºC to 500ºC. Samples for PCI measurements were prepared and loaded under controlled atmosphere conditions in a drybox. A sample size of one gram was typically used for PCI measurements. Blank absorption/desorption experiments were run each day with an empty sample chamber at the temperatures of interest (25ºC, 80ºC, 150ºC, and 400ºC) and used to correct subsequent measurements.

Metal hydride samples were purchased from Ergenics (Ringwood, NJ) and used following activation procedures recommended by the vendor. The experimental plan combines specific metal hydrides with combinations of polymer/processing method that show encouraging hydrogen storage results, in an iterative manner. Materials characterization is provided at intermediate steps in the process (Figure 2). For example, if plasma-sprayed LaRC-SI demonstrates measurable hydrogen storage, a metal hydride such as $LaNi_5$ will be combined with LaRC-SI, and the resulting blend processed by plasma spraying prior to additional PCI measurements.

Electron paramagnetic resonance (EPR) measurements were performed at 9.5-9.6 GHz (X-band) at room temperature using a Bruker ESP300E spectrometer. Powdered polymer samples were placed in quartz tubes (4 mm o.d., 3.2 mm i.d., 178 cm length). To ensure reliable intensity measurements, all tubes were filled to a constant height (~ 8 cm) such that the sample height was greater than the resonance cavity, a rectangular TE(102) cavity. A Bruker weak pitch sample (with dimensions identical to that of the samples) with a spin density of 1.13×10^{13} +/- 5% spins per centimeter was used as a standard for intensity measurements. Spectra in a set of samples were recorded using the same measurement parameters (microwave power, modulation

amplitude, receiver gain, conversion time, etc.). Double integration of the EPR spectra were carried out using the Bruker data analysis package after baseline correction.

Results and Discussion

Materials Characterization

Thermal analysis of the polymer samples showed similar results for both argon and air atmospheres. In general, the polymers showed minimal weight loss until a critical temperature was reached – above this temperature, a significant weight loss occurred. Figure 3 displays four representative TGA data sets for polyaniline, polypropylene, polytetrafluoroethylene, and LaRC-SI polyimide. From these plots, insight can be gained on the relative thermal stability of the materials, particularly when application temperatures are considered. It would be impractical to design a hydrogen storage system that operates at temperatures significantly above the critical temperature of a given polymer. For example, the polyaniline sample loses approximately 5% of its initial weight by 100ºC, followed by an additional 50% loss beginning near 200ºC. Above 400ºC, the polymer gradually loses weight at a rate of nearly 0.025% per 100ºC to 800ºC. Polypropylene and polytetrafluoroethylene undergo single, yet catastrophic, weight losses. These materials lose all of their sample weight by approximately 450ºC and 600ºC, respectively. The LaRC-SI sample exhibits the highest thermal stability of these examples, with a nominal 2% loss to 500ºC, followed by an additional 35-40% weight loss by 800ºC. Thus, the relative thermal stability of these polymers is found to be polyaniline < polypropylene < polytetrafluoroethylene < LaRC-SI. While this result is useful from a systems design perspective, it also suggests other processing influences. For example, bulk thermal processing at 400ºC is likely to modify the LaRC-SI polymer structure significantly less than the polyaniline material, because their decomposition behavior is noticeably different.

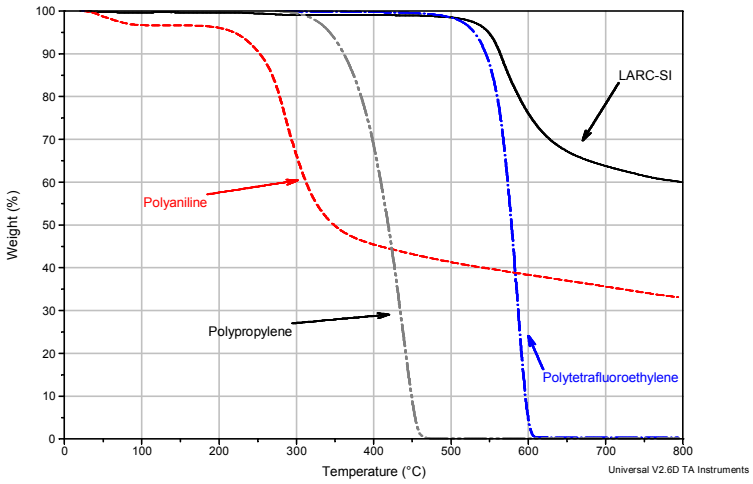

Figure 3. Representative Thermal Analysis Data for Several Polymer Samples

Changes to the polymer powder morphology are also of interest, whether induced by the processing method or by the cyclic absorption/desorption of hydrogen during the PCI

experiments. Metal hydrides typical undergo decrepitation during such cycles, but the effect of cycling on polymers is unknown. One example of morphological change induced by processing method is shown in Figure 4. Scanning electron microscopic (SEM) images of LaRC-SI powders were taken of the as-received polymer (Figure 4, left hand image) and after ball milling the polymer for two hours (Figure 4, right hand image). At least two interesting observations can be made from these images. First, the as-received powder consists of irregularly sized angular particles, many with residual bubbles on the surface. Second, the ball milling process generally reduces the particle size of the polymer and creates a more homogeneous distribution of particles.

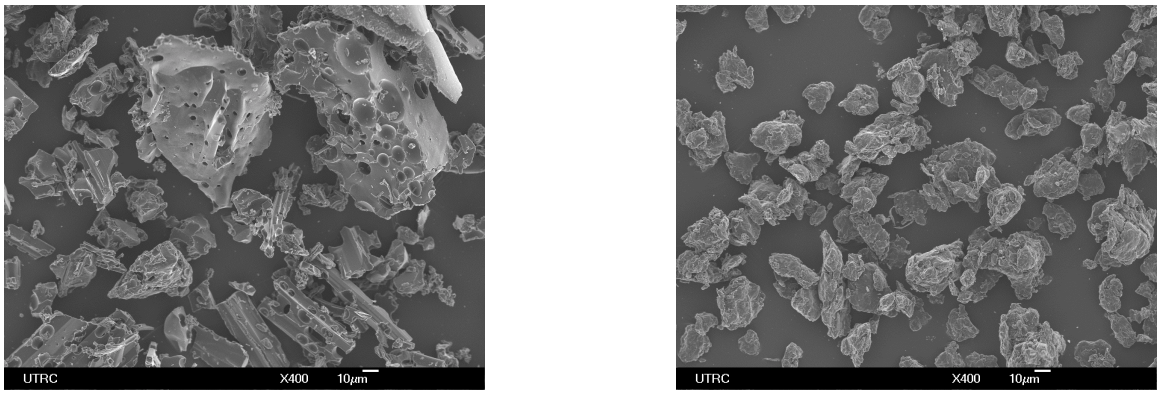

Figure 4. Representative SEM Micrographs of LaRC-SI Polymer Powders

The plasma spray process is a particularly interesting method to impart high energy into a material. Figure 5 shows a sample of LaRC-SI and 5 wt% TiH_2 undergoing the plasma spray process – the intense energetics of the process are readily apparent, and small, glowing particles can be seen at the end of the particle stream. A close-up view of the nozzle is also shown.

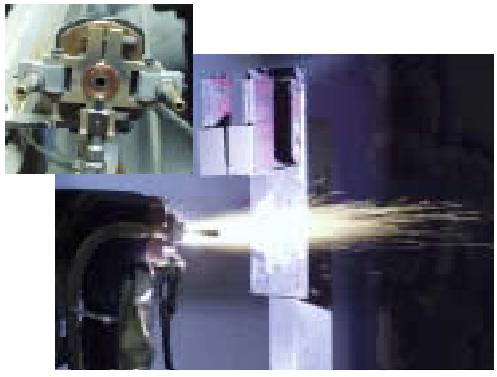

Figure 5. Plasma Spraying of LaRC-SI/5% TiH_2; Nozzle Geometry Shown in Inset

Although thermal, mechanical and plasma-spray processing offer unique means to combine polymers and metal hydride powders, the actual nature of the interactions between the phases, as

well as the location of each phase, is unclear. For example, in a PDMH consisting of LaRC-SI and TiH_2, it would be beneficial to determine the location of each phase within the composite, as well as any differences imparted by the various processing methods. To examine this issue, a blended powder containing 95 wt% LaRC-SI and 5 wt% TiH_2 was prepared. This sample was plasma sprayed and examined by conventional SEM and using backscattered electrons (BSE). Figure 6 shows the results of this analysis. The left hand image of Figure 6 shows a typical SEM micrograph of the plasma sprayed sample. In comparison to the image in Figure 4 of the as-received polymer, the plasma sprayed sample contains more rounded particles – suggesting that the particles have partially deformed, perhaps by melting, in the plasma. The right hand image of Figure 6 is a back scattered image of the same sample region, and distinguishes atomic weight differences. Specifically, particles containing the heavier Ti appear brighter in the image. It is apparent that a larger particle containing Ti is not in close proximity to a polymer particle (right side of right hand image), while a smaller Ti-containing particle is embedded within a polymer particle. The relationship between polymer and metal hydride interparticle spacing and hydrogen storage is not known at this time, but certainly worthy of further study.

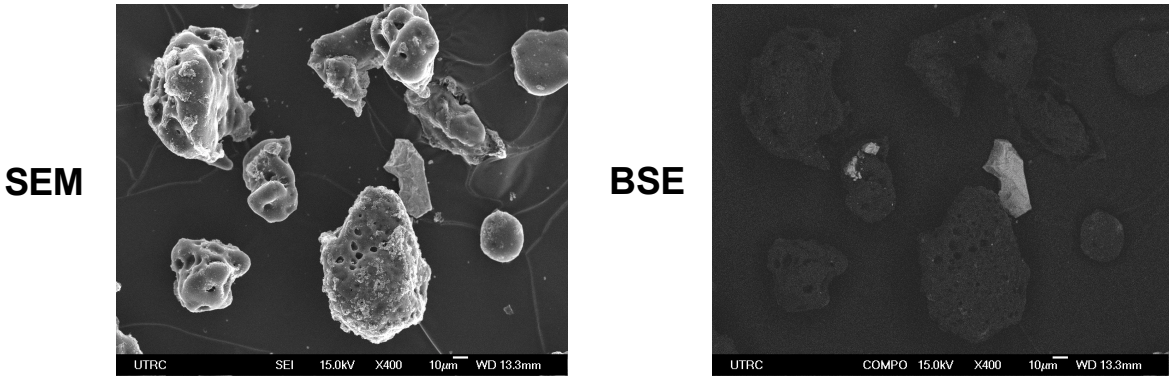

Figure 6. Representative SEM Micrographs of Plasma Sprayed LaRC-SI/5% TiH_2

Hydrogen Storage Measurements

Preliminary PCI measurements on plasma-sprayed blends of LaRC-SI and 5 wt% TiH_2 were performed at Advanced Materials Corporation at 300ºC and 400ºC. These relatively high temperatures were chosen in attempts to reproduce data shown in Figure 1 (TiH_2 and Polymer 3 + TiH_2). Although these temperatures are required to achieve significant hydrogen absorption in TiH_2, they are unsuitable for use in PEM-based fuel cells, which typically require application temperatures of 80ºC to 120ºC. The data presented in Figure 7 summarize two absorption/desorptions cycles at 400ºC and one cycle at 300ºC. Note that the maximum stored hydrogen content is about 0.36 wt%, which nicely confirms the data in Figure 1, but which falls far short of the DOE goal of 5.5 wt%. Hysteresis is also noticeable between the absorption and desorption stages of the cycle, becoming smaller with increased cycling and lower temperatures. One possible explanation for the observed hysteresis is a thermally-induced structural change in the polymer or the metal hydride phase.

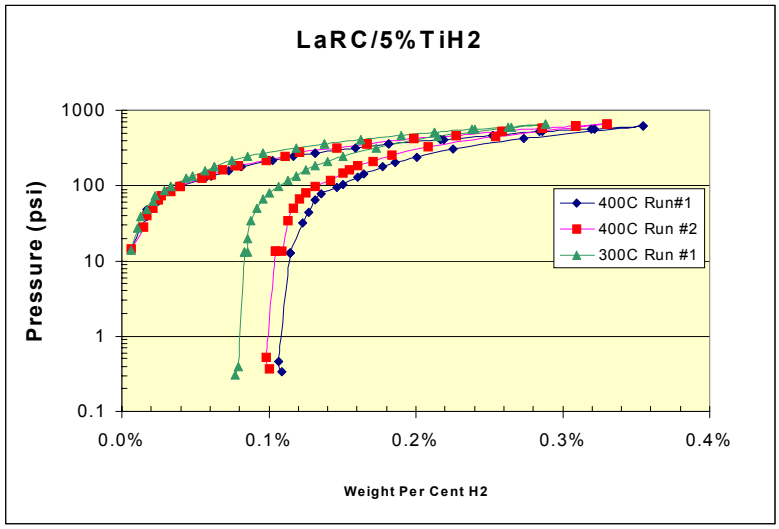

Figure 7. Initial PCI Data for Plasma Sprayed LaRC-SI/5% TiH_2

Over 50 additional PCI measurements (absorption and desorption cycles) were performed at UTRC since these initial data were acquired. Specifically, PCI data were obtained for as-received polymers at 25ºC, 80ºC, 150ºC, and 400ºC; for 2 hour ball milled samples at 25ºC and 150ºC; for 400ºC processed polymers at 25ºC; and for several plasma sprayed polymers at 25ºC. To date, within experimental error and reproducibility limits, no processed polymer sample has shown measurable hydrogen storage capacity that differs significantly from the blank sample holder. As examples, Figure 8 shows two PCI curves of a blank sample holder and plasma-sprayed Nylon 6 polyamide sample. Both data sets were acquired at UTRC at room temperature. Note that the Y-axis displays pressure of applied hydrogen gas, in atmospheres, and the X-axis reflects the amount of hydrogen ab/desorbed, in weight percent. There is virtually no difference between the data sets. Similar results have been achieved with essentially all of the polymer samples in the absence of metal hydride.

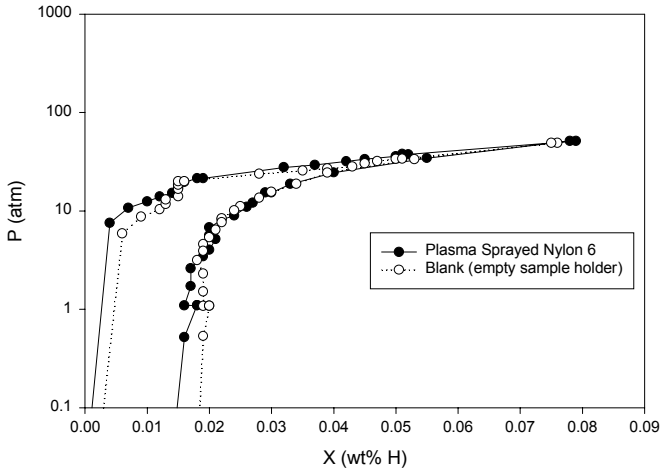

Figure 8. Typical UTRC PCI Data

Electron Paramagnetic Resonance (EPR) Measurements

Preliminary EPR measurements (not shown) on as-received and plasma-sprayed LaRC-SI indicated that the as-received material had a relatively low signal intensity compared to the plasma-sprayed material. Qualitatively, these measurements implied that the plasma spray process altered the polymer structure and created a population of free radical sites through bond scission. Additional work was performed in an effort to quantify the density of free radicals created by the various processing methods. Quantitative experiments were performed on as-received and several processed LaRC-SI samples, although under different conditions. Figure 9 summarizes these experiments. The series of curves shows relative intensity versus magnetic field for the processed samples. The integrated intensity of the signal increased in this order: as received (2.82 $x10^{15}$ spins/gram) < 150ºC sample (3.49 $x10^{15}$ spins/gram) < 2 hour ball milled sample (2.44 $x10^{16}$ spins/gram). Note that the LaRC-SI sample shows little thermal degradation by 400ºC (Figure 3), suggesting that loss of hydrogen atoms may not be a significant source of free radicals. To date, the EPR spectrum of the plasma sprayed sample has not been acquired, but it is expected to show significantly higher free radical concentration than the other samples due to the high energy of the plasma spray process.

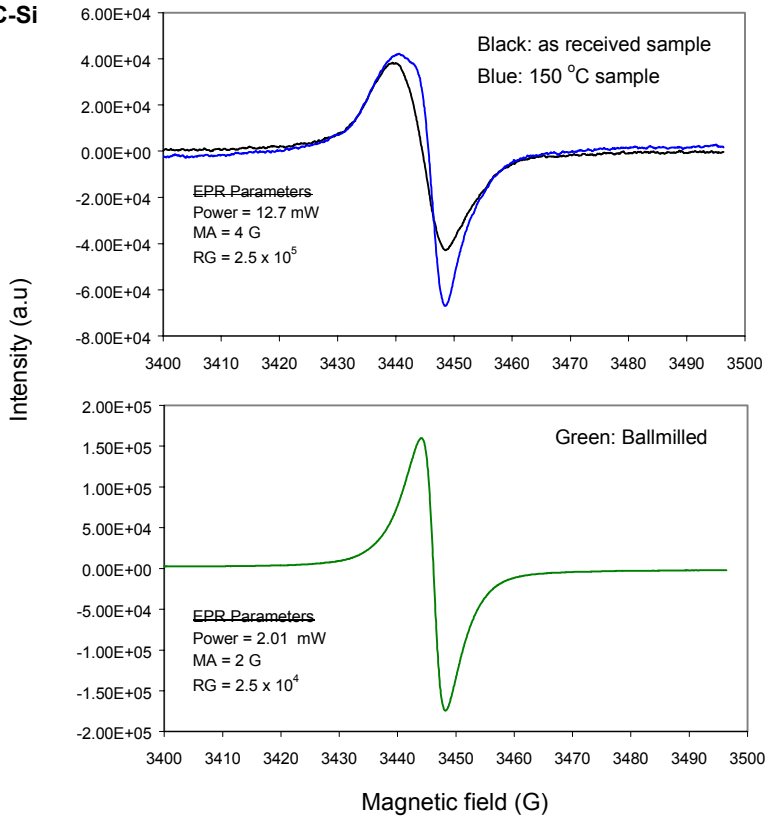

Figure 9. Representative EPR Data for Processed LaRC-SI Polyimide Samples

Figure 10 summarizes a similar experimental study for Kapton, and does not include quantified plasma spray data. The as-received sample and a sample processed at 150ºC show similar spin densities of 1.24 x 10^{16} spins/gram of sample. Kapton thermally processed at 400ºC or ball-

milled for 2 hours, shows measurably higher spin densities of 4.83 x 10^{16} spins/gram and 8.01 x 10^{16} spins/gram, respectively. In general, the measured spin densities of the Kapton samples were significantly higher than the LaRC-SI samples, suggesting differences in structural robustness between the two polymers.

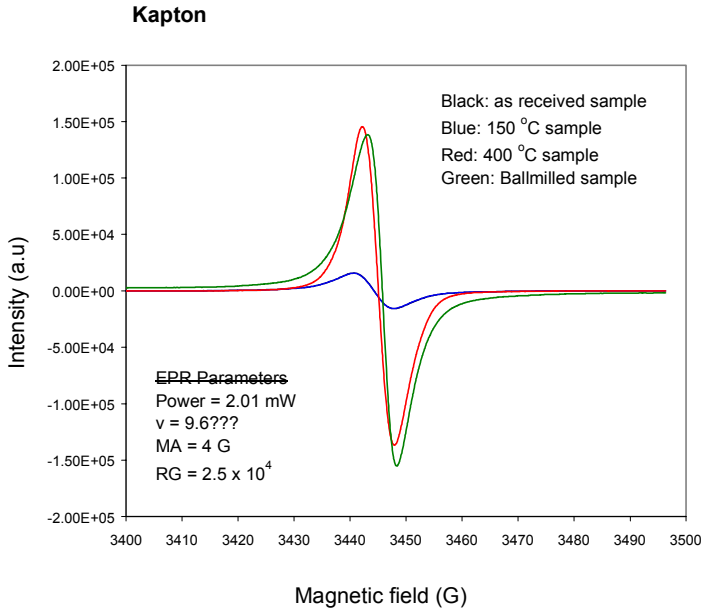

Figure 10. Representative EPR Data for Processed Kapton Polyimide Samples

While it is evident that choice of processing method can influence the resulting chemical structure of the polymer, the relationship with a polymer's initial or modified structure, and its ability to store hydrogen or interact with the metal hydride, is not clear at this time. These topics will comprise the focus of future efforts.

Hydrogen Storage Mechanisms in Polymers

The exact role, if any, that a polymer plays in modifying the hydrogen storage capacity of a metal hydride is unknown at this time. While no significant evidence for storage enhancement has been found to date, it is plausible that a polymer structure could interact with molecular hydrogen. Given that each polymer sample contains a high concentration of hydrogen covalently bonded to the polymer structure, it is conceivable that hydrogen species could interact on a molecular level. For example, depending on the charge of the hydrogen species, a combination of covalent, ionic, metallic, H-bonding and van der Waals interactions could exist within and between the polymer chains and/or with the metal hydride. Free radicals present within the polymer structure could further participate in hydrogen movement through the polymer network. Figure 11 provides a schematic diagram hypothesizing the role of the polymer. With Kapton polyimide as the polymer example, this study has shown that plasma spray processing introduces a significant free radical population into the sample. Although the exact location of the free radical sites has yet to be determined (but can be specifically assigned based on the EPR spectral

characteristics), they can be represented as dangling bonds, denoted in red in Figure 11. As a hydrogen molecule diffuses near a dangling bond, it can dissociate into two hydrogen atoms, which can further interact with the polymer free radical to form a covalent bond, or diffuse into the metal hydride lattice. Of course, the actual surface chemistry of the metal hydride must be considered in this example. The yellow inset box implies that the metal surface is populated by various oxide, hydroxide, water, or adsorbed diatomic hydrogen species – each will influence the incorporation of hydrogen atoms into the structure. The reversibility and thermodynamic stability of the covalent bond, newly created between hydrogen atom and the polymer, must also be considered. Nevertheless, Figure 11 presents one possible scenario for the role of polymers.

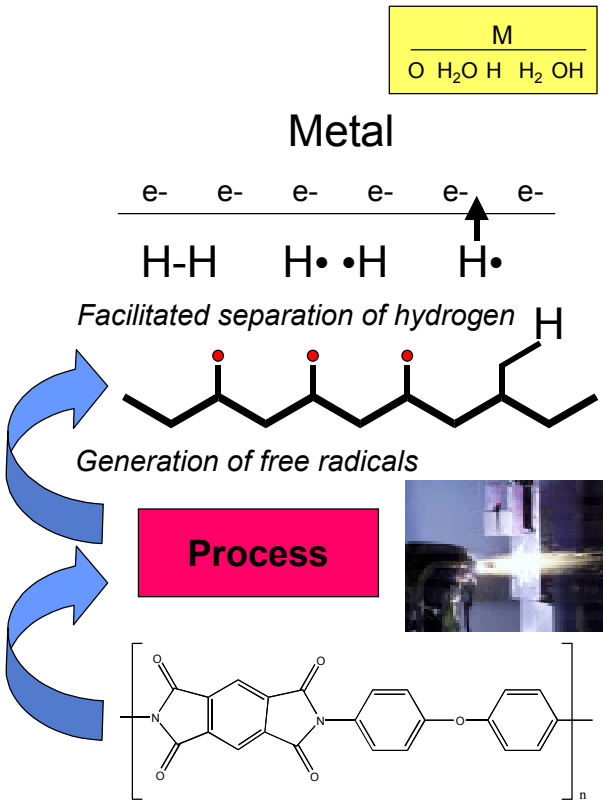

Figure 11. Possible Relationship Between Free Radicals and Hydrogen in PDMH

Conclusions

Dispersion of metal hydrides into low-density polymers, capable of storing hydrogen, is a unique approach to meeting the energy storage requirements of fuel cell powered automobiles. UTRC has begun to explore materials and processing design space to elucidate mechanisms of hydrogen storage in PDMH systems. To date, there is little experimental evidence to support the notion that polymers alone provide significant hydrogen storage capacity. Work continues to examine the inter-relationship between the dispersed metal hydride and the polymer support phase, and the resulting hydrogen storage behavior of the composite. In particular, the microstructural

distribution of metal hydride and polymer phases, and the effect of homogeneity on performance at a given temperature, must be determined.

EPR spectroscopic techniques have proven valuable in confirming and quantifying the amount of free radicals in processed polymer samples. The role free radicals play in hydrogen storage remains unclear, however, but reinforces the need to better understand the molecular interactions between metal hydride and polymer phases. The thermal stability of the polymer phase, relative to the operation temperature of the fuel cell, is also a critical consideration when designing a PDMH-based hydrogen storage system.

Future Work

Ongoing efforts are focused towards completing the EPR spectral measurements on all plasma-sprayed polymer samples. Additional PCI experiments, at various temperatures, are similarly planned for the plasma-sprayed polymers. Following assessment of the 'best' combination of processing method and polymer, select mixtures of polymer and $LaNi_5$ and Mg_2Ni will be prepared and processed accordingly. The hydrogen storage capacity of these optimized composite samples will be measured between room temperature and 150ºC. The effects of varying the polymer/metal hydride composition ratio will also be investigated.

Assuming that sufficient hydrogen storage capacity is measured for the optimized samples, a qualitative systems design will be developed to account for weight, volume, cost and thermal requirements of a commercial PDMH approach.

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References

DeLuchi, M. A., 1992. In: *Hydrogen Fuel-Cell Vehicles*, Institute of Transportation Studies, UC Davis.

Dillon, A. C., Jones, K. M., Bekkedahl, T. A., Kiang, C. H., Bethune, D. S., and Heben, M. J. 1997 *Nature*, 386:377.

Jarvi, T. D., Dec. 15, 1999. *Hydrogen Storage in Polymer Dispersed Metal Hydrides*, UTRC Proposal P.300.0024 in response to U. S. DOE Solicitation DE-PS36-00GO10482.

Meinzer, R. A., U. S. Patent 5,360,461 Nov. 1, 1994. *Polymeric Storage Bed for Hydrogen.*

Willard, H. H., Merritt, L.L., Dean, J. A., and Settle, F. A. 1981. *Instrumental Methods of Analysis, Sixth Edition (Chapter 12).* Stamford; Wadsworth Publishing Co.