

IV.H.5 Elucidation of Hydride Interaction Mechanisms with Carbon Nanostructures and the Formation of Novel Nanocomposites

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Objectives

- Continue to support the office of Basic Energy Sciences mission through the development of a basic understanding of the formation and the physiochemical properties of carbon nanostructures, formed by the interaction of carbon nanomaterials with hydrides and/or hydrogen gas.
- Obtain knowledge that allows us to control material properties at the electronic, molecular, and atomic level which will serve as the foundation of new energy technologies that can support other aspects of DOE missions.
- Utilize a simple solvent-assisted method, developed during previous work, to intercalate carbon nanomaterials with metal using metal hydrides to form a desired metallo-fullerides (M_x-C_{60}) with specific stoichiometries.
- Based on preliminary results from previous work, these novel materials can have unique hydrogen storage, electronic properties and high ionic mobility.
- The proposed work is aimed at examining how the presence or absence of hydrogen in these materials can affect its physical and chemical properties which will allow us to “fine-tuning” the properties of the material.

Technical Barriers

- The ability to disperse metal atoms uniformly in a carbon nanostructure is necessary in order to reliably synthesize composites with uniform properties on small and large scales.

- Little experimental information about the mechanism of hydrogen interaction with un/doped carbon nanostructures is available.
- Initial studies on the hydrogenation of carbon nanostructures have shown that the physical and chemical properties of the material can be significantly altered and controlled.
- Advances in atomic scale imaging (i.e. scanning tunneling microscopy [STM], transmission electron microscopy [TEM]) have shown that morphological changes at the atomic scale can affect the properties of the bulk material.

Abstract

This program will continue to support the office of Basic Energy Sciences mission. A simple method, relying on metastasis reaction between hydrides and carbon nanostructures to precisely achieve desired stoichiometries will be employed to form novel metal-fulleride nanocomposites with unprecedented properties. Our preliminary results indicated that these metal-fulleride nanocomposites interact with hydrogen reversibly at temperatures well below the precursor components used in forming the nanocomposites. The preliminary data showed a tremendous *enhancement of mobility* of species such as hydrogen and alkali metals in a solid electrolyte made of $LiBH_4$ and C_{60} [1]. The hydrogen binding energy in the hydride allows the exchange of elemental metal to form homogenous structures. Commonly used material characterizations techniques (e.g. TEM, SEM/energy dispersive X-ray, X-ray diffraction [XRD], neutron scattering, raman spectroscopy [NMR]) will provide information on morphology, composition, crystal structure, vibration spectra, ionic mobility and nature of bonding. Thermodynamic measurements will be used to obtain basic understanding of the formation of these nanocomposites and their interaction with hydrogen. Computer controlled thermogravimetric, volumetric analyzers, and DSC will also be used in this study.

Our study is aimed at attempting to predict and control material properties at the electronic, atomic, and molecular level that can be the foundation of new energy technologies and can support other aspects of DOE missions.

The proposed research is performed as ONE TASK organized around the following four integrated activities:

- Activity 1: Synthesis and Characterization of M_x -Fullerene Materials

- Activity 2: Investigation of Ionic Mobility Enhancement and Alteration of Electronic Properties
- Activity 3: Investigation of the Properties of Carbon Nanostructures Modified With Non Metallic Elements
- Activity 4: Atomistic Modeling of Metal Doped Carbon Nanostructures

Progress Report

This research work is aimed at obtaining a fundamental understanding of the nanoscale level of hydrogen sorption behavior of metal-doped carbon nanostructures. It is well established that the doping or intercalation of carbon nanomaterials with metal atoms has a significant impact on the chemical and physical properties of the resulting material. Furthermore, the physical and chemical properties of these materials are extremely sensitive to the identity of the added metal(s) as well as its molar ratio with the carbon nanomaterial. The experimental work is closely linked to relevant modeling studies of these materials [2]. Advances in hydrogen storage technology based on pure carbon nanostructures and particularly metal-doped carbon nanostructures require the development of a basic understanding of their physicochemical properties and the manner in which these properties influence the hydrogen bonding. Our effort is focused on the understanding of the hydrogen interaction mechanisms such as physisorption, weak covalent bonding, and chemisorption in these nanocarbon systems.

Our recent efforts have focused on the synthesis and characterization of a lithium doped C_{60} material that can reversibly store and release hydrogen via a chemisorption mechanism. Through a systematic series of experiments it was determined that a material synthesized with a 6:1 ($Li:C_{60}$) mole ratio can absorb the highest weight percent of hydrogen (~5 wt %). Spectroscopic characterization of the material revealed that it resembles a hydrogenated fullerene (i.e. *fullerane*), however, the material can store and release hydrogen at much milder conditions than an undoped C_{60} sample.

NMR characterization demonstrated that hydrogen atoms are associated with both Li and C and indicates that the presence of Li in the material dictates the hydrogen absorption sites. Interestingly, there is a reversible phase change observed for C_{60} doped with lithium in the XRD measurements. When the material is hydrogenated at 350°C and 105 bar H_2 , a phase change from face-centered cubic (*fcc*) to body-centered cubic (*bcc*) is observed in the material. Upon dehydrogenation the material returns to its original *fcc* structure. The 7Li MAS NMR also suggests that upon rehydrogenation a Li atom may actually go inside the fullerene cage as indicated by the upfield resonance (~10 ppm).

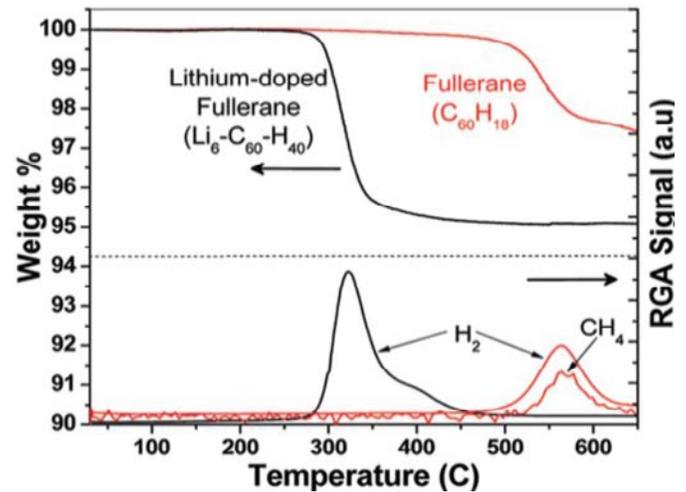


FIGURE 1. Thermogravimetric analysis (TGA)-residual gas analysis (RGA) comparison of the fourth desorption of the $LiH:C_{60}$ (6:1) sample (black) and hydrofullerene (red). The materials were hydrogenated at 350°C under 105 bar H_2 for 11 h. The colors of the RGA signals correspond to the TGA signal.

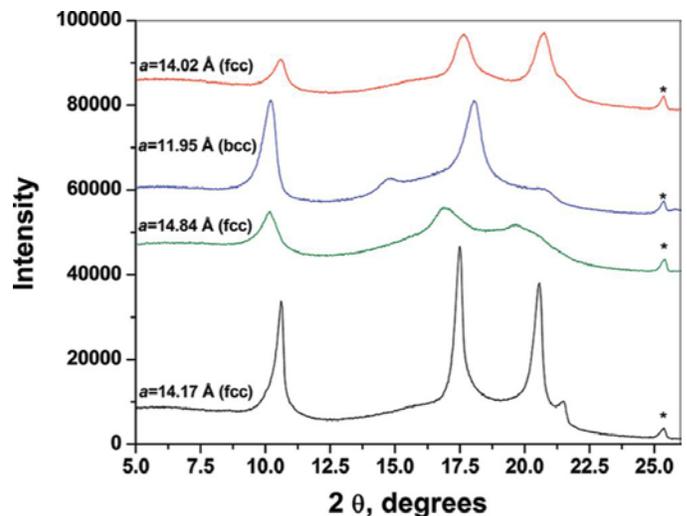


FIGURE 2. XRD stack plot of $LiH:C_{60}$ (6:1) during the hydrogen desorption/absorption experiments. Black, as prepared; green, after third rehydrogenation (250°C, 105 bar H_2); blue, after third rehydrogenation (350°C, 105 bar H_2); and red, after third dehydrogenation. The (*) is a peak from the Al_2O_3 internal standard.

We have also demonstrated that the intercalation of C_{60} with sodium (via NaH) results in almost identical hydrogen storage behavior, via a similar mechanism. The material was subject to 10 desorption/absorption cycles and demonstrated a reversible capacity of ~2.5 wt% H_2 through the reversible formation of a sodium doped fullerene.

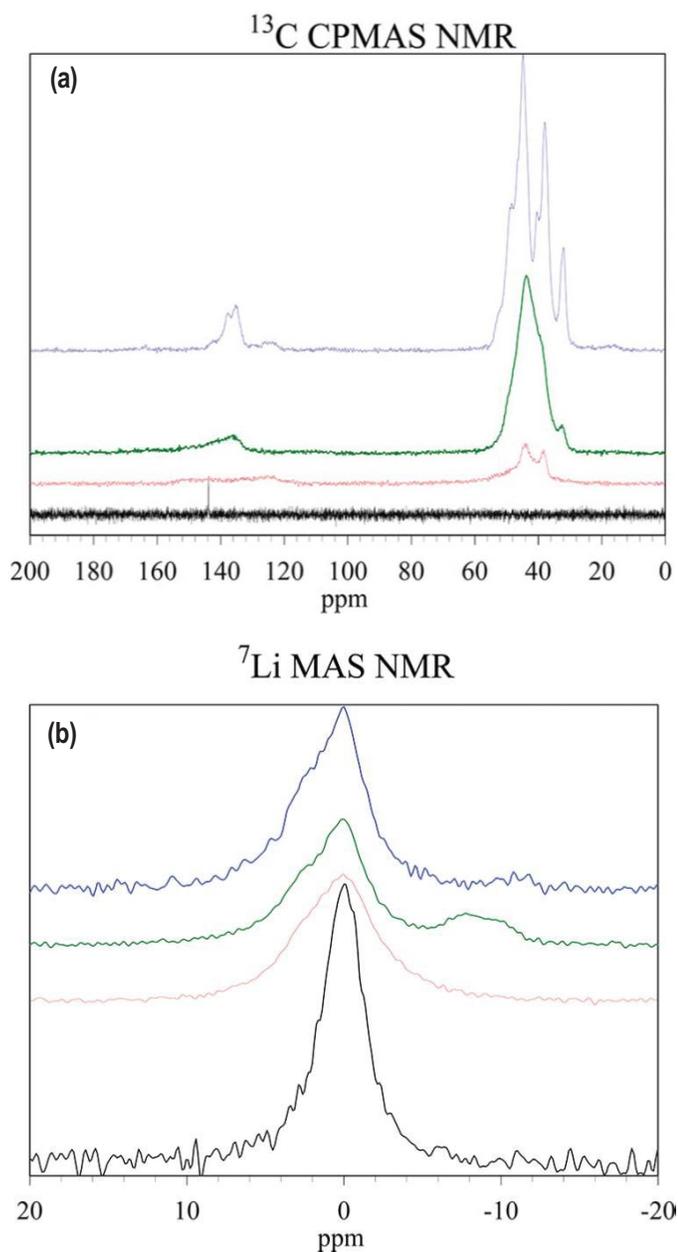


FIGURE 3. All of the samples are of the LiH:C60 (6:1) material: black, as prepared; red, third dehydrogenation; green, third rehydrogenation (250°C, 105 bar H₂), and blue, third rehydrogenation (350°C, 105 bar H₂). (a) ^{13}C MAS NMR; (b) ^7Li MAS NMR. Samples were spun at 15 kHz under dry N₂ gas.

Future Directions

Our current interests include atomic scale imaging utilizing the scanning probe microscopy facility at the Center for Nanoscale Materials to get atomic scale imaging of the material at various states of hydrogenation. Utilizing the facility's ultra-high vacuum atomic force microscopy/scanning tunneling microscopy, we will gain a fundamental understanding of the physical and chemical properties of carbon nanostructures or composites. We have been allotted two weeks of instrument time to perform our experiments in Fiscal Year 2012. We are also collaborating with Prof. Rosario Cantelli of Sapienza University of Rome to perform anelastic spectroscopy of Li and Na intercalated C₆₀ materials at different states of hydrogenation. This technique can be used to quantitatively determine the dynamics and the diffusion parameters of mobile species in solids and the occurrence of phase transitions, including chemical reactions. We are currently preparing samples for neutron diffraction experiments. This will allow us to determine the structure of the metal intercalated C₆₀ as well as the preferential binding sites for hydrogen in the material.

References

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2. P.A. Berseth, A.G. Harter, R. Zidan, A. Blomqvist, C.M. Araujo, R.H. Scheicher, R. Ahuja, P. Jena, *Nano Letters*, **2009**, *9*, 1501-1505.

Publications (including patents) acknowledging the grant or contract

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3. J.A. Teprovich Jr., M. Wellons, R. Lascola, S. Hwang, P. Ward, R. Compton, R. Zidan. *Nano Letters*, **2012**, *12*, 582-589.

Patents

1. R. Zidan, M.S. Wellons High Capacity Hydrogen Storage Nanocomposite Materials patent application filed
2. R. Zidan, J.A. Teprovich, H. Colon-Mercado, Novel Nano-Composite Electrodes for Hybrid Lithium-Ion Battery patent application filed