

Elucidation of Hydride Interaction Mechanisms with Carbon Nanostructures and the Formation of Novel Nanocomposites

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Savannah River National Laboratory



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Team and Collaborators



Savannah River National Laboratory Team:

Dr. Joe A. Teprovich Jr., Dr. Doug A. Knight, Dr. Matthew S. Wellons, Dr. Lucile C. Teague, Dr. Robert Lascola, Joseph Wheeler

NMR measurements and analysis: in Collaboration with Prof. Mark S. Conradi, Washington Univ. of St. Louis and Dr. Son-Jong Hwang, California Institute of Technology

Theoretical analysis and modeling of nanocomposites : in Collaboration with Prof. Puru Jena, Virginia Commonwealth University

Mass Spectrometry, Prof. Robert N. Compton, University of Tennessee

Anelastic Spectroscopy, Prof. Rosario Cantelli, University of Rome

Neutron Measurements, Jacque Huot (UQTR) and Bjorn Hubback (IFE)

Atomic Scale Imaging, Center for Nanoscale Materials (Argonne National Lab.)

Objectives

Original Objectives

- Investigate the formation, decomposition, and mechanism of hydrogen interaction with a novel class of carbon nanostructures and complex hydrides
- Studying these systems is useful to understand the formation of novel carbon- metal nano structures and helps to understand the effect of confinement in carbon scaffold
- Theoretical and experimental investigation of a variety of *carbon nanostructures* (CNT, MWCNT, fullerenes, etc.) as well as *complex metal hydrides* (NaAlH_4 , LiBH_4 , LiAlH_4 , etc.) for hydrogen storage

The work, however, led to Identifying new composite materials with

New Objectives:

Determine how they interact reversibly with hydrogen, physical and chemical properties, determine microcrystalline structure and mechanisms

Advances in Materials Development for Hydrogen Storage

- **composites made out of C_{60} and hydrides**

- $Li-C_{60}-H$, $LiBH_4-C_{60}$, $LiAlH_4-C_{60}$, $Na-C_{60}-H$, $NaAlH_4-C_{60}$

Experimental Design:

Carbon Nanostructure

Complex Metal Hydride

mixing
Intercalation
(B.M.-free)

**Intercalated
Material**
(hydrogenated)

(desorption)

$- H_2$

**Intercalated
Material**

(dehydrogenated)

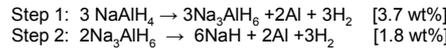
$+ H_2$
(absorption)

Hydrogen capacity?
Reversibility?
Mechanism?

Fundamental Studies on Hydrogen Interaction with Carbon Nanostructures led to the identification of novel materials based on carbon nanostructures

NaAlH₄ and Carbon Nanostructures

Sodium Aluminum Hydride (NaAlH₄)

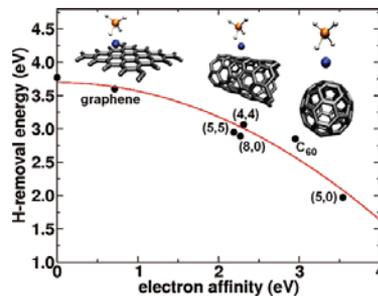


Experimental Results

- Nanocomposites of NaAlH₄ with various carbon sources (graphite, CNT, and C₆₀) were synthesized by a ball-mill free procedure
- Cycling experiments of the composites (abs/des) showed that C₆₀ was superior to other carbon sources tested
- C₆₀ also lowered the desorption temperature of NaAlH₄ to ~130°C (from ~180°C, uncatalyzed)

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

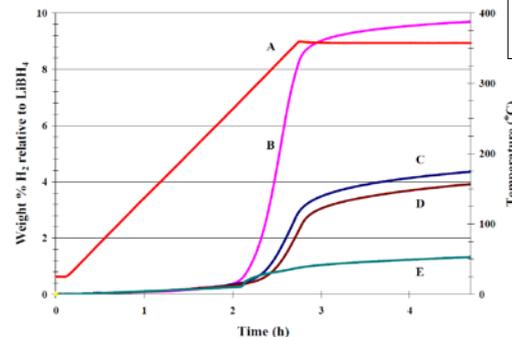
Theoretical Results



Increase in electron affinity decreases the H-removal energy (inductive effect)

LiBH₄-C₆₀ Nanocomposite

Lithium Borohydride (LiBH₄)

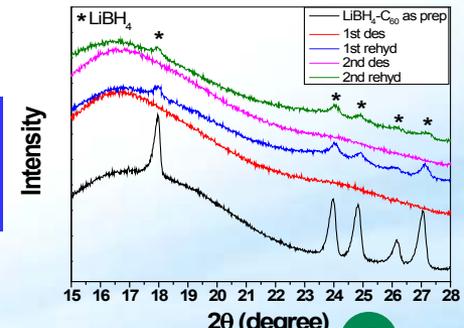


(A) T ramp (2°C/min); LiBH₄:C₆₀ (1.6 mol%); (B) 1st desorption; (C) 2nd desorption; (D) 3rd Desorption; (E) LiBH₄ standard

- Reversible hydrogen storage has been demonstrated by ball-milling LiBH₄ with MgH₂ and TiCl₃
- Reversible hydrogen storage has also been observed for LiBH₄ with nanoporous carbon scaffolds, activated carbon, and SWNT's

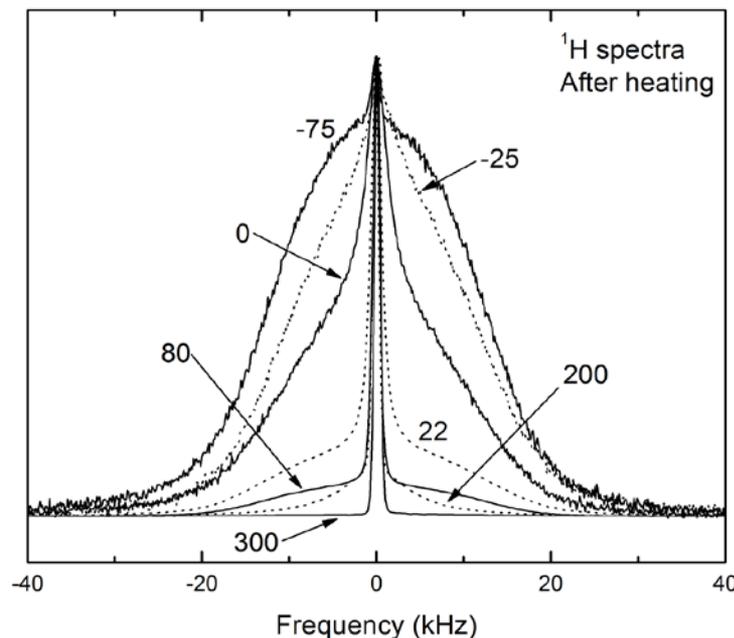
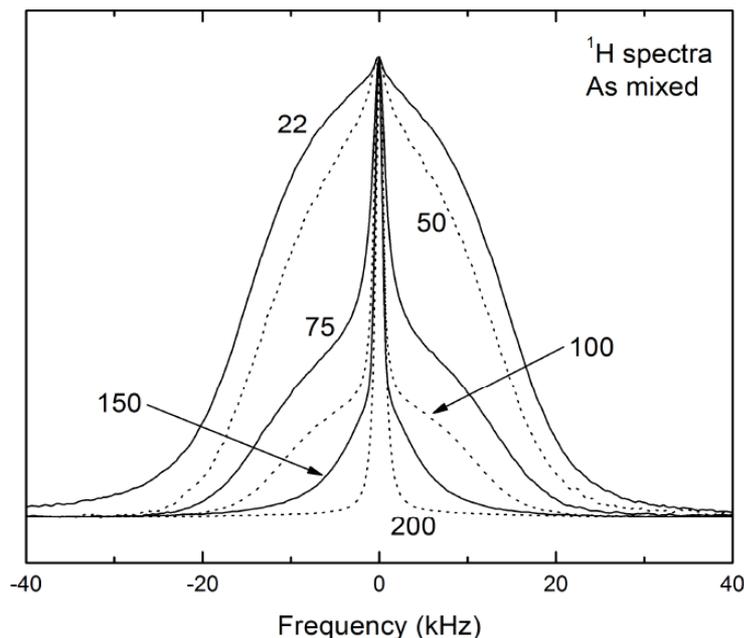
Nanocomposites of LiBH₄ with C₆₀ demonstrates increased desorption kinetics and reversible rehydrogen (4.2 wt% H₂)

XRD confirms the reversible formation of LiBH₄ in the nanocomposite over multiple cycles



Vajo, J.; Skeith, S.; Mertens, F. *J. Phys. Chem. B* **2005**, *109*, 3719
 Gross, A.; Vajo, J.; Atta, S.; Olson, G. **2008**, *J. Phys. Chem. C* *112*, 5651
 Fang, Z-Z; Wang, P.; Rufford, T.; Kang X-D; Lu G-Q; Cheng H-M. **2008**, *Acta Mater*, *56*, 6257
 Wang, P-J; Fang Z-Z; Ma L-P; Kang, X-D; Wang P. *Int. J Hydrog. Energy*. **2008**, *33*, 5611
 Wellons, M. S.; Berseth, P. A.; Zidan, R. *Nanotechnology* **2009**, *20*.

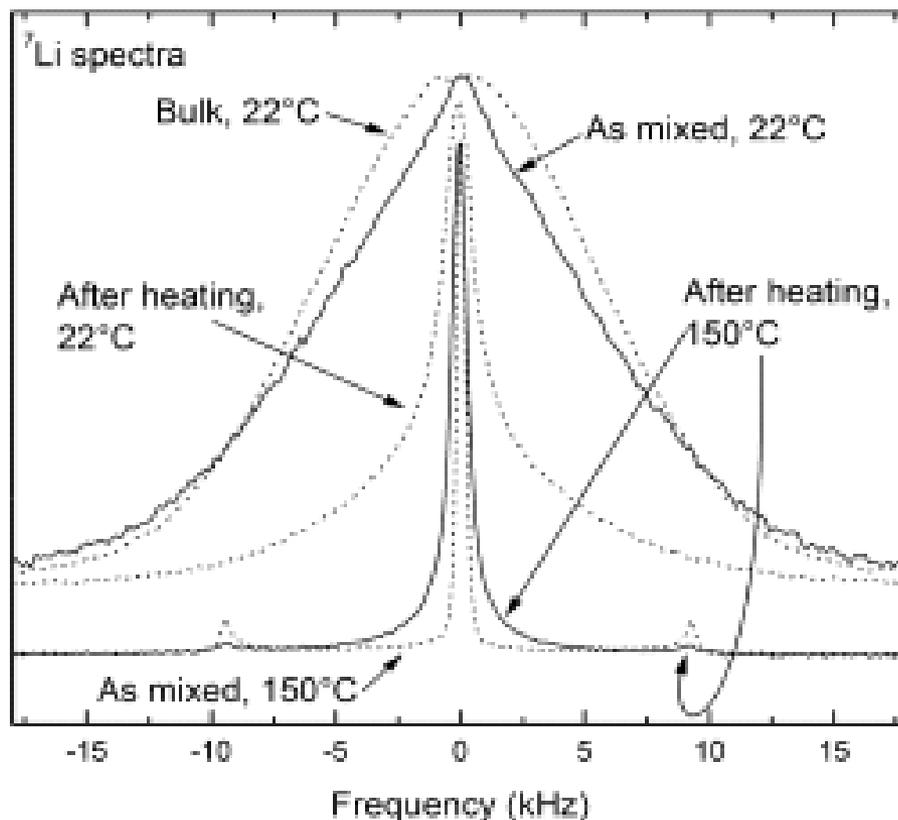
Variable Temperature NMR ($LiBH_4-C_{60}$)



- Heating $LiBH_4-C_{60}$ increases the fraction of mobile hydrogen (as BH_4^-) as well as lithium ions in the nanocomposite material
- After heating, 1H spectra is similar to a $LiBH_4$ impregnated aerogel that was reported by Conradi *et al.*
 - The fraction of mobile BH_4^- at 22°C in the $LiBH_4-C_{60}$ material (36%) is approximately double the amount of mobile BH_4^- in a previously reported $LiBH_4-C_{60}$ material

In Collaboration with Prof. Mark S. Conradi, Washington Univ. in St. Louis

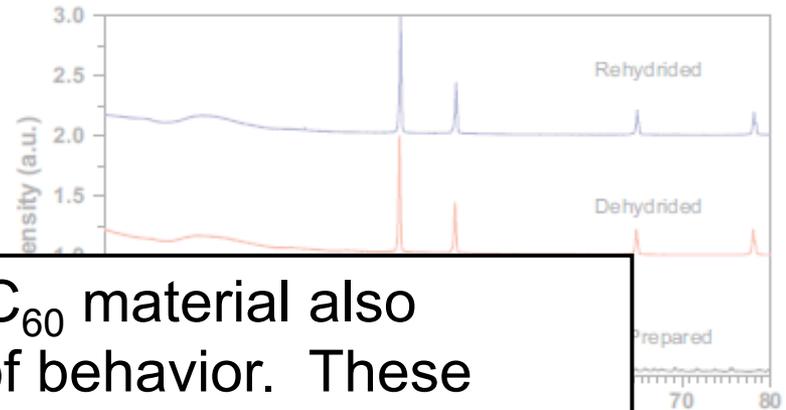
Variable Temperature NMR ($LiBH_4-C_{60}$)



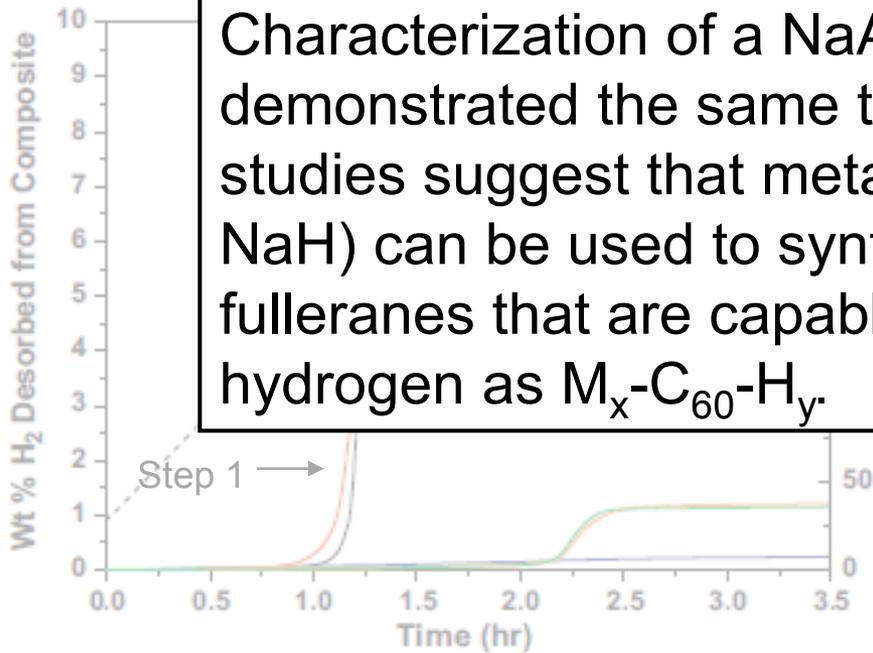
In Collaboration with Prof. Mark S. Conradi, Washington Univ. in St. Louis

Lithium Aluminum Hydride (LiAlH₄)

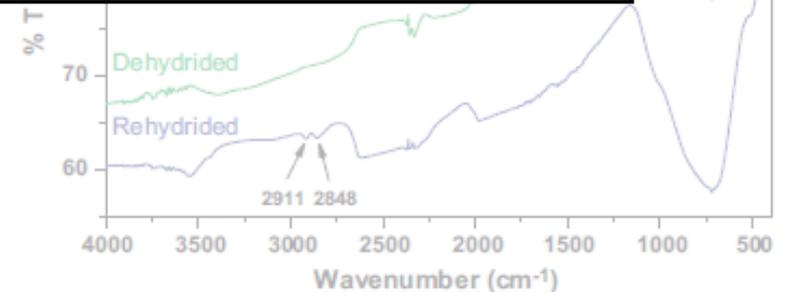
- Step 1: 3LiAlH₄ → Li₃AlH₆ + 2Al + 3H₂ [5.3 wt%]
 Step 2: Li₃AlH₆ → 3LiH + Al + 3/2H₂ [7.9 wt% total]
 Step 3: LiH → Li + 1/2H₂ [10.5 wt% total]



Characterization of a NaAlH₄-C₆₀ material also demonstrated the same type of behavior. These studies suggest that metal hydrides (i.e. LiH and NaH) can be used to synthesize intercalated fulleranes that are capable of reversibly storing hydrogen as M_x-C₆₀-H_y.



Rehydrogenation at 350 C and 100 bar H₂ for 11 hours
 LiAlH₄ standard (black) , 2nd desorption (blue),
 LiAlH₄:C₆₀ (60:1)- 1st desorption (red), 2nd (green),
 3rd (orange).



▪ The two peaks at 2848 and 2911 cm⁻¹ indicate the formation of **C-H bonds**. This suggests the formation of a hydrogenated fullerene (*fullerane*). Suggests active storage material is Li_x-C₆₀-H_y.

Synthesis and Characterization of a Lithium-Doped Fullerene ($\text{Li}_x\text{-C}_{60}\text{-H}_y$) for Reversible Hydrogen Storage

Joseph A. Teprovich, Jr.,[†] Matthew S. Wellons,[†] Robert Lascola,[†] Son-Jong Hwang,[‡] Patrick A. Ward,[§] Robert N. Compton,[§] and Ragaay Zidan^{*†}

[†]Clean Energy Directorate, Savannah River National Lab, P.O. Box A, Aiken, South Carolina 29808, United States

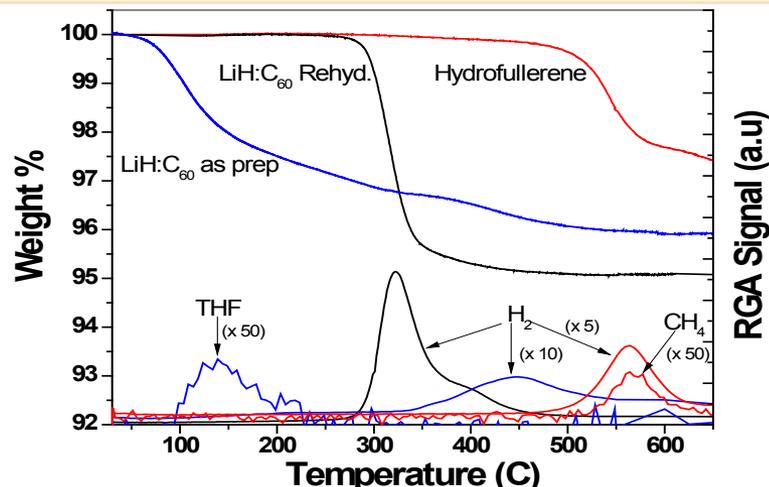
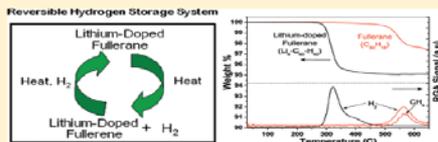
[‡]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States

[§]Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States

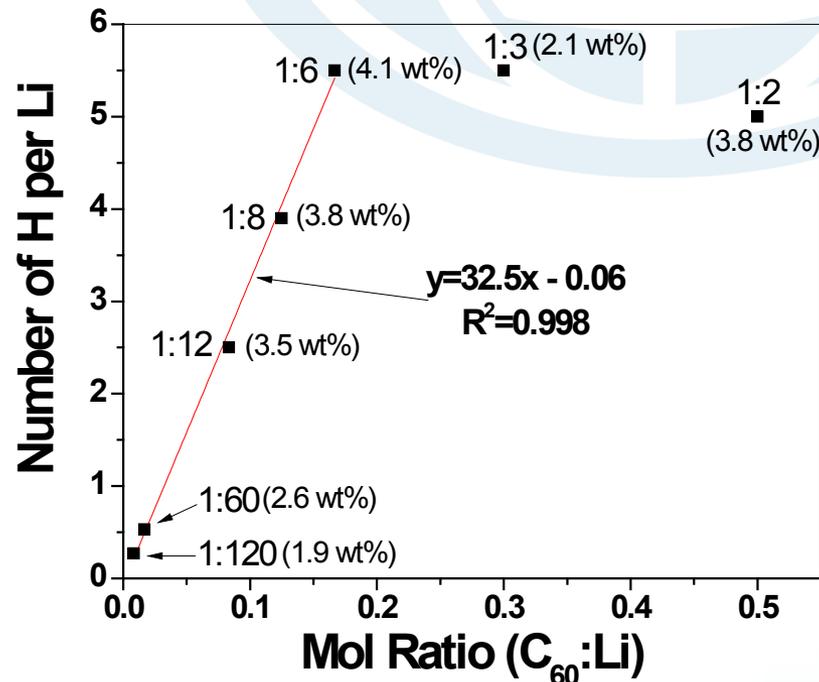
Supporting Information

ABSTRACT: Herein, we present a lithium-doped fullerene ($\text{Li}_x\text{-C}_{60}\text{-H}_y$) that is capable of reversibly storing hydrogen through chemisorption at elevated temperatures and pressures. This system is unique in that hydrogen is closely associated with lithium and carbon upon rehydrogenation of the material and that the weight percent of H_2 stored in the material is intimately linked to the stoichiometric ratio of $\text{Li}:\text{C}_{60}$ in the material. Characterization of the material (IR, Raman, UV-vis, XRD, LDI-TOF-MS, and NMR) indicates that a lithium-doped fullerene is formed upon rehydrogenation in which the active hydrogen storage material is similar to a hydrogenated fullerene. Under optimized conditions, a lithium-doped fullerene with a $\text{Li}:\text{C}_{60}$ mole ratio of 6:1 can reversibly desorb up to 5 wt % H_2 with an onset temperature of $\sim 270^\circ\text{C}$, which is significantly less than the desorption temperature of hydrogenated fullerenes (C_{60}H_x) and pure lithium hydride (decomposition temperature 500–600 and 670°C respectively). However, our $\text{Li}_x\text{-C}_{60}\text{-H}_y$ system does not suffer from the same drawbacks as typical hydrogenated fullerenes (high desorption T and release of hydrocarbons) because the fullerene cage remains mostly intact and is only slightly modified during multiple hydrogen desorption/absorption cycles. We also observed a reversible phase transition of C_{60} in the material from face-centered cubic to body-centered cubic at high levels of hydrogenation.

KEYWORDS: Hydrogen storage, metal hydride, fullerene, fullerane, metal-doped C_{60}



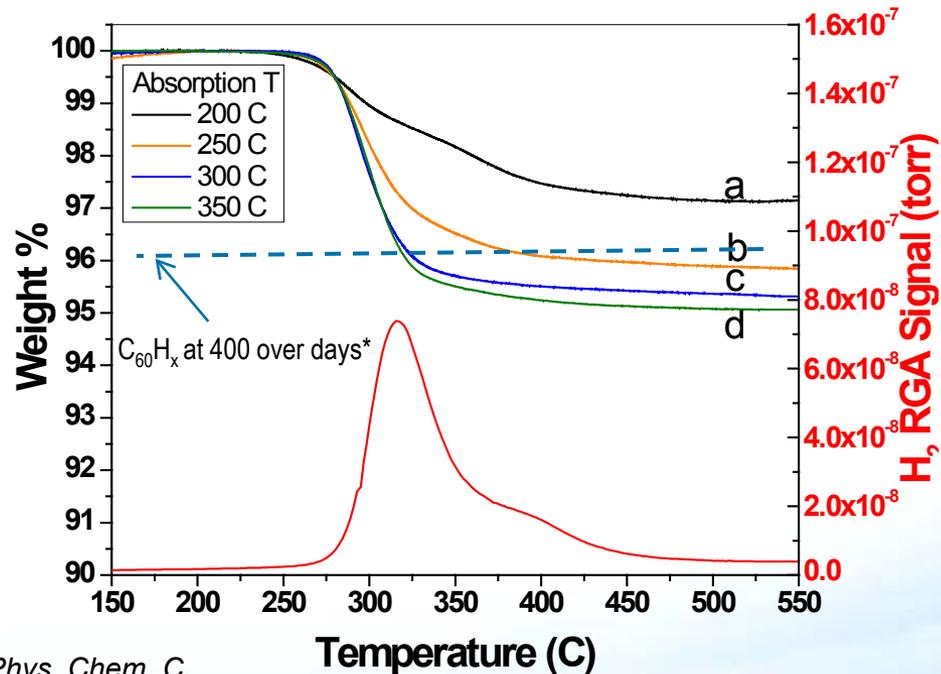
TGA-RGA comparison of our $\text{Li}_6\text{-C}_{60}\text{-H}_{40}$ nanocomposite (as prepared and rehydrogenated) with a pure hydrofullerene. Our material is higher in capacity and releases only pure H_2 and no methane like the hydrofullerene. The samples were rehydrogenated under 105 bar H_2 at 350°C for 11 hr



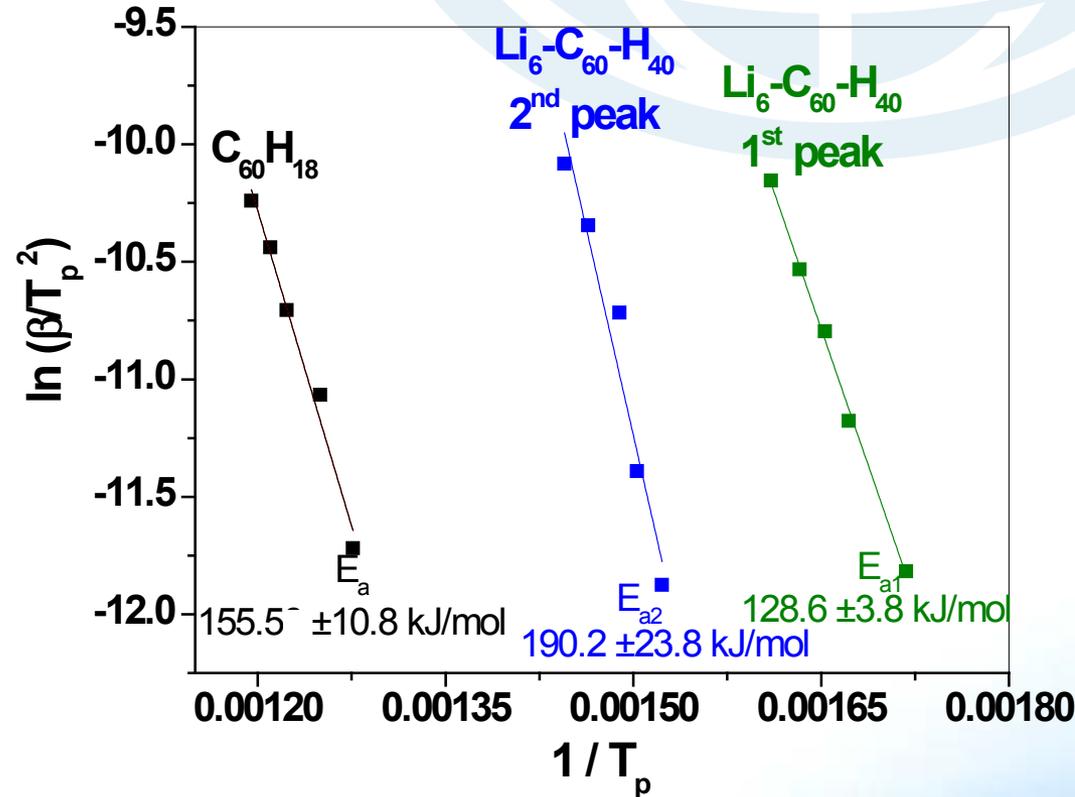
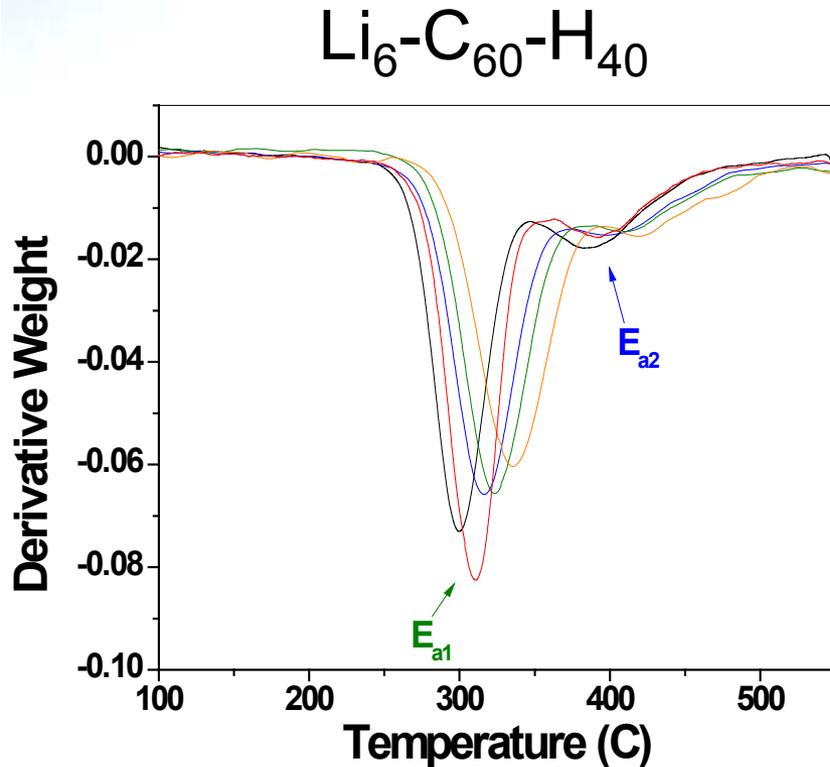
Optimization of the $\text{C}_{60}:\text{Li}$ ratio for hydrogen storage. Samples were hydrogenated under 105 bar H_2 at 250°C for 11 hr

Effect of T and P on the H₂ Capacity of the 6:1 Ratio

Rehydrogenation Pressure (bar H ₂)	Rehydrogenation Temp. (C)	Observed H ₂ wt % ^a	Ave. Value of y for Li ₆ -C ₆₀ -H _y ^b
25	350	1.8	14
50	350	2.9	23
75	350	4.1	33
105	200	2.8	22
105	250	4.1	33
105	300	4.6	37
105	350	5.0	40



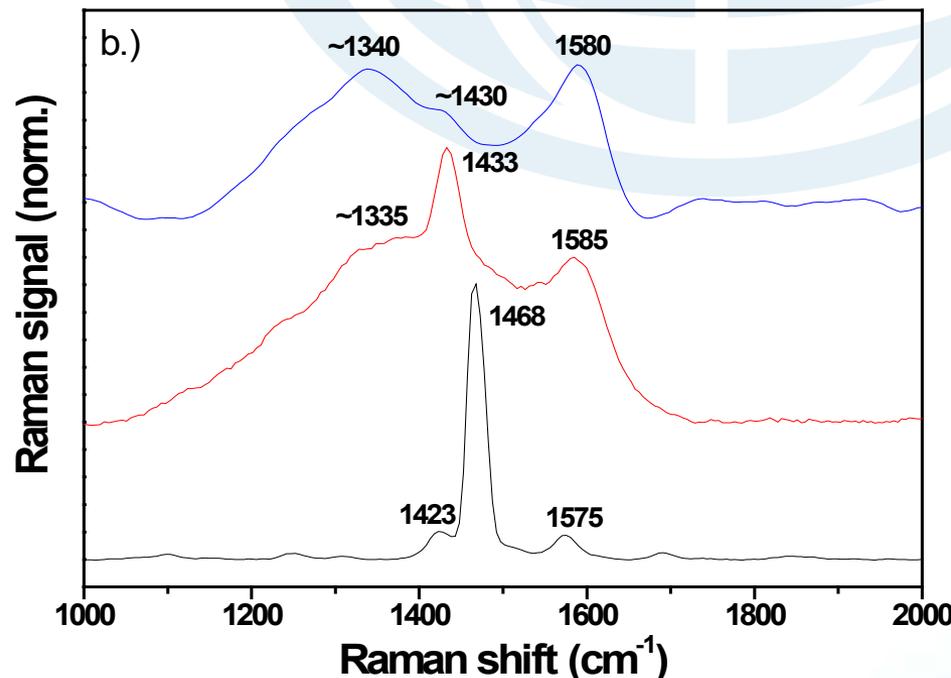
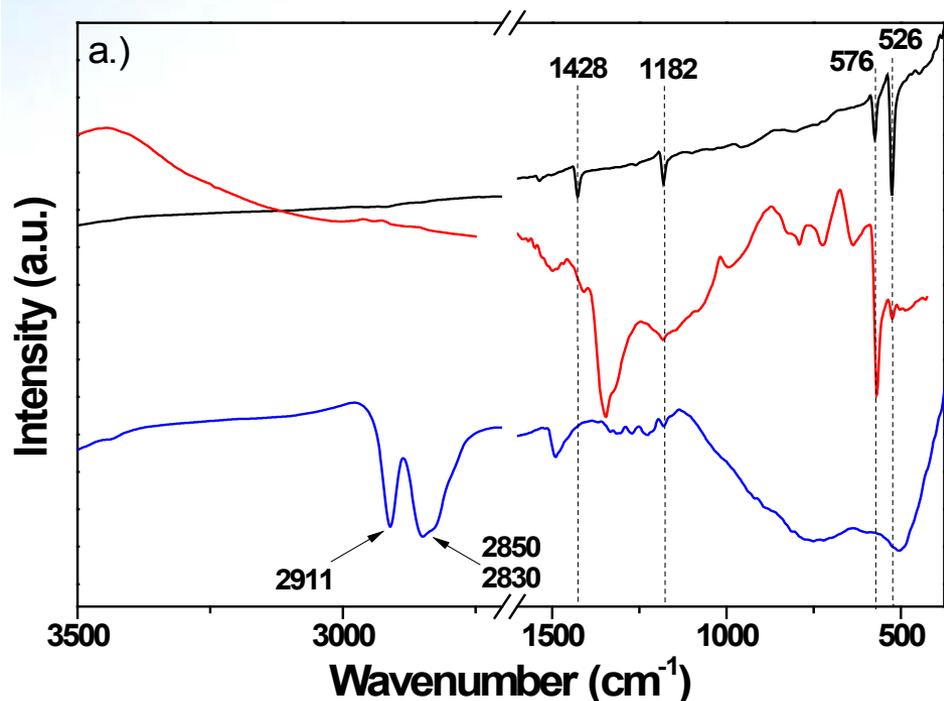
Activation Energy (Kissinger Plot)



Reduction in the activation energy for the onset of H_2 desorption is lowered by 26.9 kJ/mol upon the intercalation of lithium.

IR and Raman (Where is the Hydrogen?)

Red- Dehydrogenated (x3), Blue- Rehydrogenated (x3, 350°C), Black- as prepared

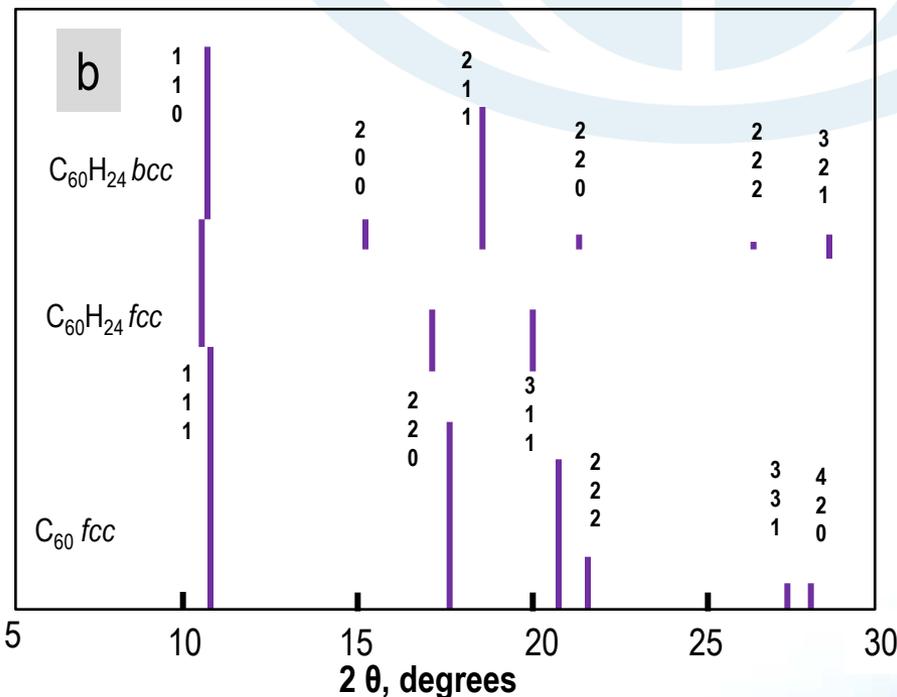
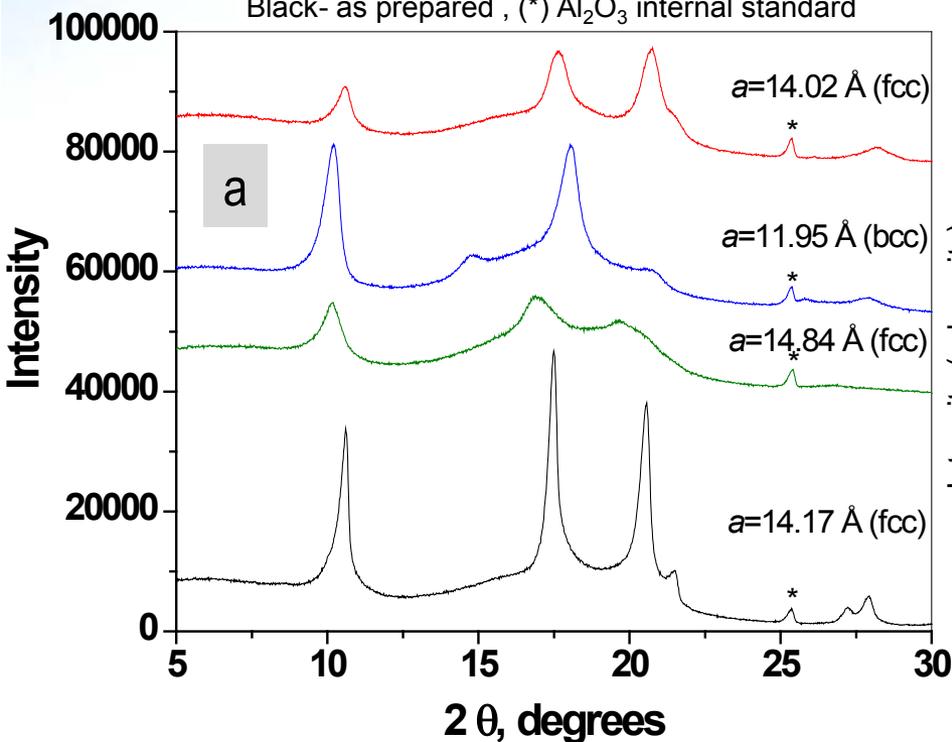


- Formation of C-H bonds is confirmed by the presence of the 3 peaks that form between 2800-3000 cm⁻¹.
- The C=C stretching vibration (1428 cm⁻¹) is shifted to ~1344 cm⁻¹ and is sensitive to the degree of charge transfer to the C₆₀ as well as to polymerization. (i.e. K₆C₆₀ – 1341 cm⁻¹ and photopolymerized C₆₀ - 1324 cm⁻¹)

- Upon dehydrogenation there is a shift of the A_g mode from 1468 to 1433 cm⁻¹ and is consistent with a 6 electron transfer to C₆₀ (6 cm⁻¹ per e⁻)
- The appearance of broad bands at ~1335 and ~1585 cm⁻¹ is consistent with polymerization and/or cage modification

XRD Depicting Phase Transformation

Red- Dehydrogenated (x3)
 Blue- Rehydrogenated (x3, 350°C)
 Green- Rehydrogenated (x3, 250°C)
 Black- as prepared , (*) Al₂O₃ internal standard

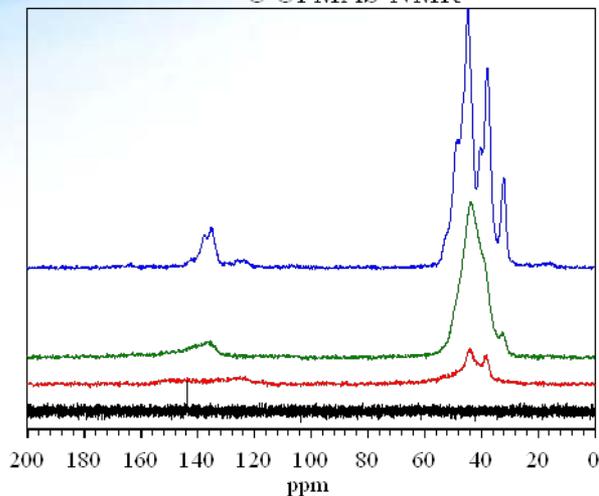


A phase reversible phase transition from *fcc* to *bcc* occurs depending on the temperature at which the hydrogenation is performed. This typically will not happen until the C₆₀ is exposed to extremely high pressures (~3 GPa)

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

V.E. Antonova, I.O. Bashkina, S.S. Khasanova, A.P. Moravskyb, Yu.G. Morozovc, Yu.M. Shulgab, Yu.A. Ossipyany, E.G. Ponyatovsky, *Journal of Alloys and Compounds* 330-332 (2002) 365-368

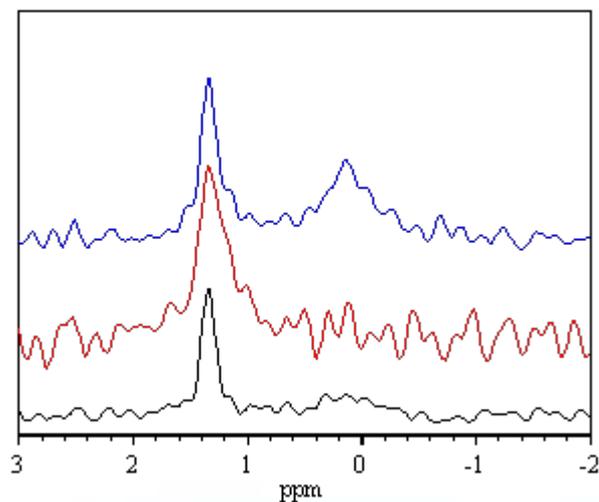
^{13}C CPMAS NMR



After the rehydrogenation, the sp^3 carbons now grew significantly and reach to about 50% for the sample rehydrogenated at 350 °C, meaning 38 out of 60 carbons are in the sp^3 side due to the hydrogenation. Interestingly, peaks for both sp^2 and sp^3 for the sample rehydrogenated at 250 °C look broader and ill defined, indicating that the sample hydrogenated at 250 °C could be in the process of transitioning from fcc to bcc.

Red- Dehydrogenated (x3)
Blue- Rehydrogenated (x3, 350 C)
Green- Rehydrogenated (x3, 250 C)
Black- as prepared

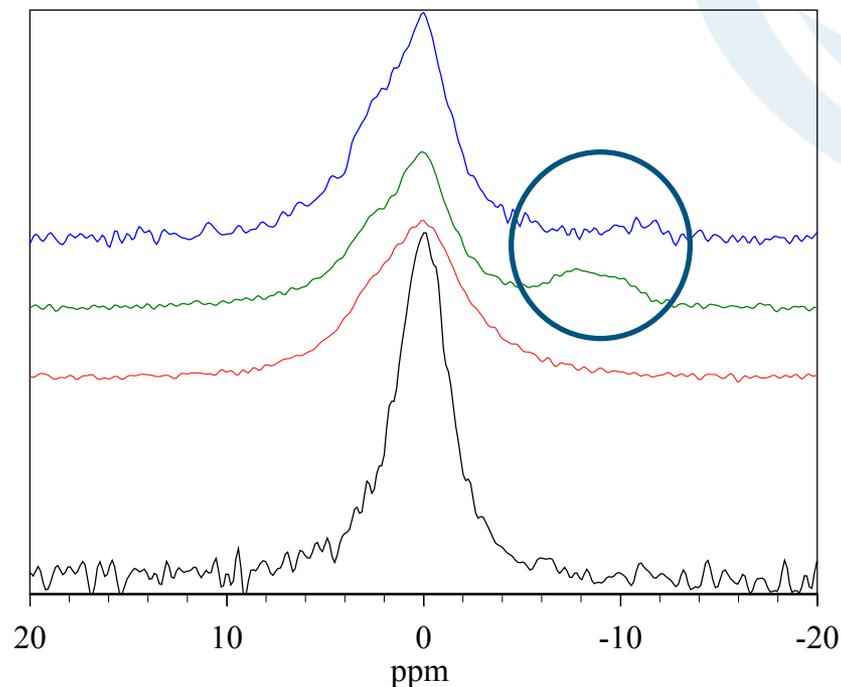
^6Li CPMAS NMR



Cross-polarization (CP) [Vaugh *et al.*] can be used to enhance the signal of nuclei with a low gyromagnetic ratio by magnetization transfer from nuclei with a high gyromagnetic ratio (e.g. ^1H),

The CPMAS of ^6Li also shows that hydrogen is closely associated with lithium in order to get a signal in the CP

^7Li MAS NMR



Red- Dehydrogenated (x3)
Blue- Rehydrogenated (x3, 350°C)
Green- Rehydrogenated (x3, 250°C)
Black- as prepared

Unusual far upfield shift at -9.1 and -11.5 ppm in the ^7Li MAS NMR spectra of the rehydrogenated samples, and indicates that a highly shielded Li species is formed during the rehydrogenation process. This was previously observed in a $\text{Li}@C_{60}$ and a Li-corannulene structure *,**.

* Zabula, A. V.; Filatov, A. S.; Spisak, S. N.; Rogachev, A. Y.; Petrukhina, M. A. *Science*, 2011, 333, 1008–1011

** Aoyagi, S.; Nishibori, E.; Sawa, H.; Sugimoto, K.; Takata, M.; Miyata, Y.; Kitaura, R.; Shinohara, H.; Okada, H.; Sakai, T.; Ono, Y.; Kawachi, K.; Yokoo, K.; Ono, S.; Omote, K.; Kasama, Y.; Ishikawa, S.; Komuro, T.; Tobita, H. *Nat. Chem.* 2010, 2, 678–683

Na₆-C₆₀ Material

Na₆C₆₀

10 Desorption Cycles of of 1:6 C60:NaH

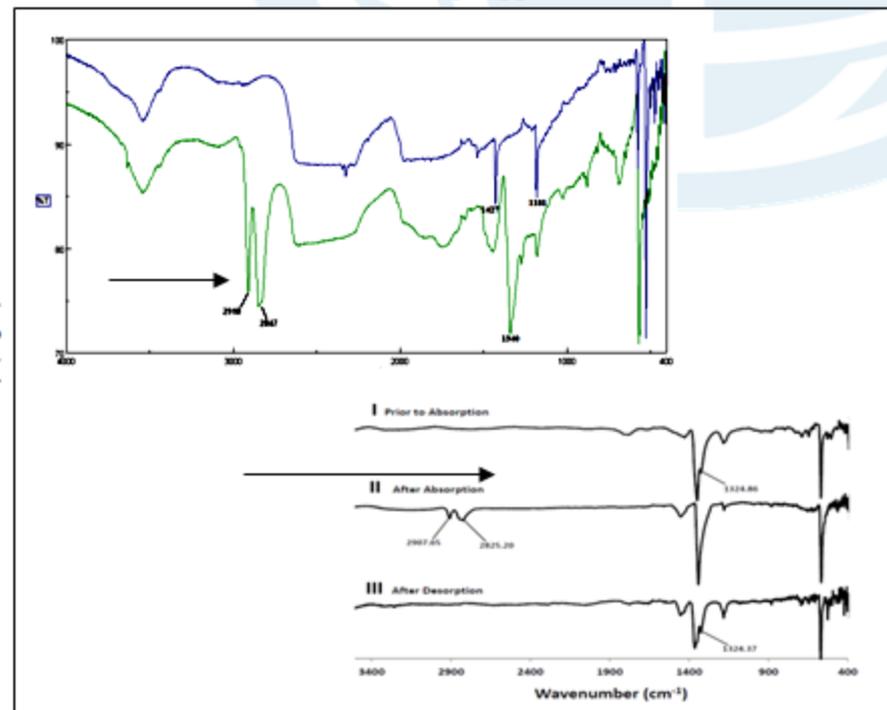
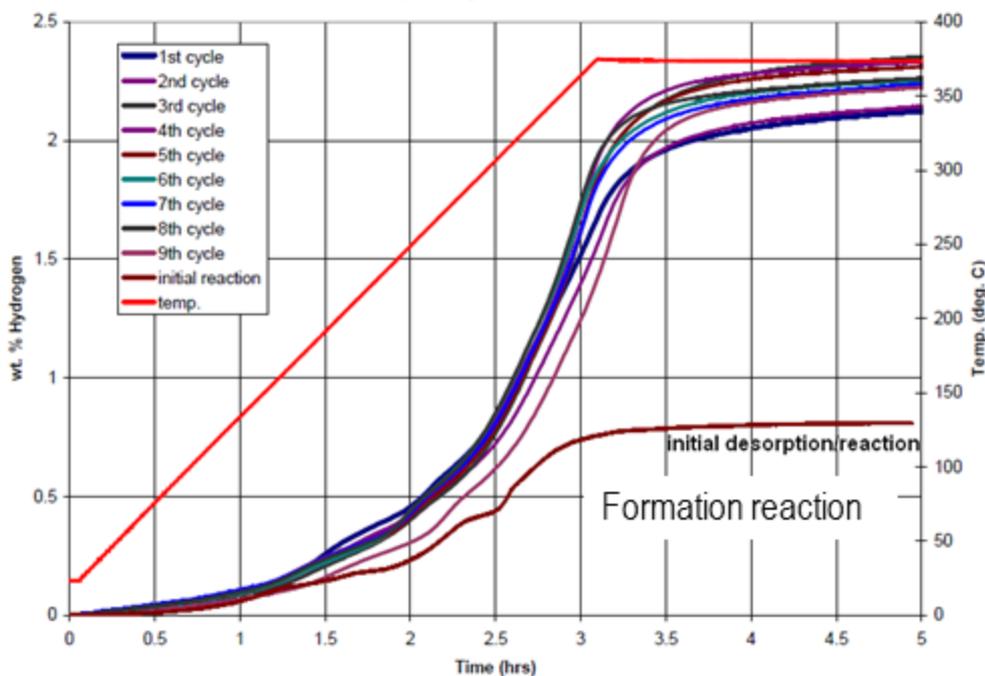
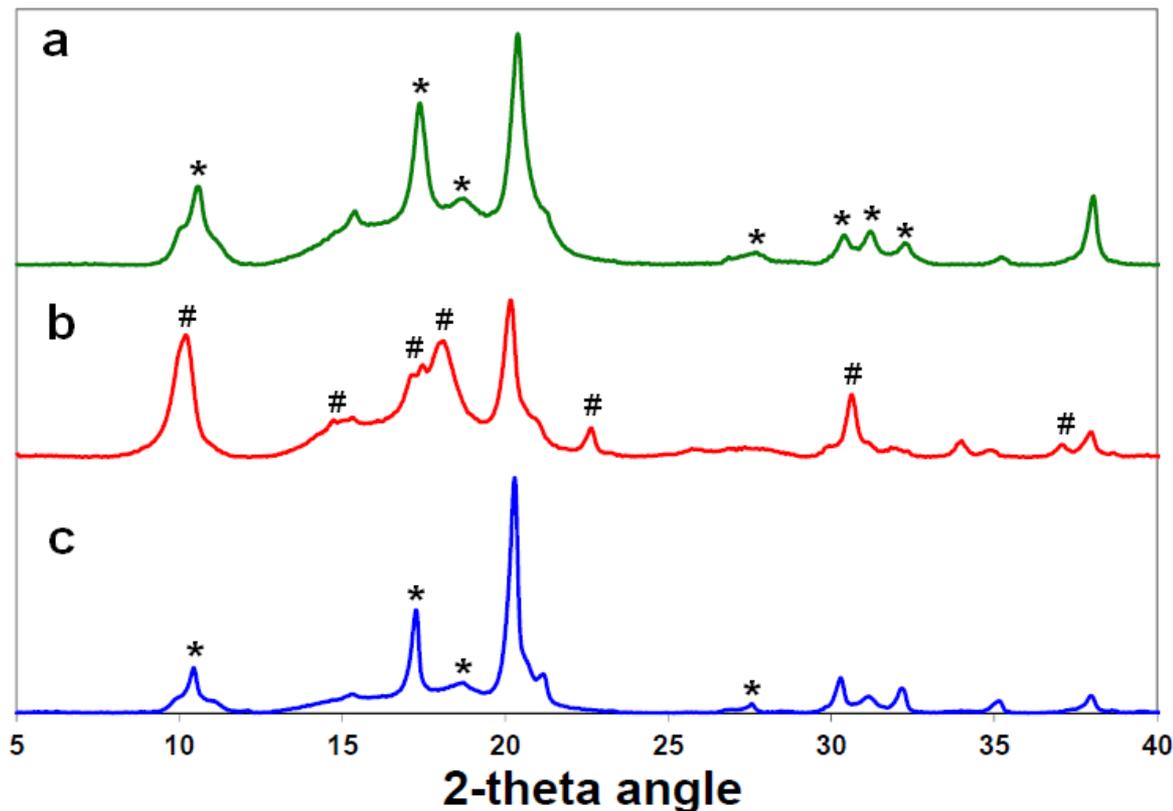


Figure shows FT-IR stack plot of the Na₆-C₆₀ system. Upon rehydrogenation, the appearance of the peaks at -2907-2910 and 2825-28470 cm⁻¹ indicates the formation of C-H bonds on the fullerene.

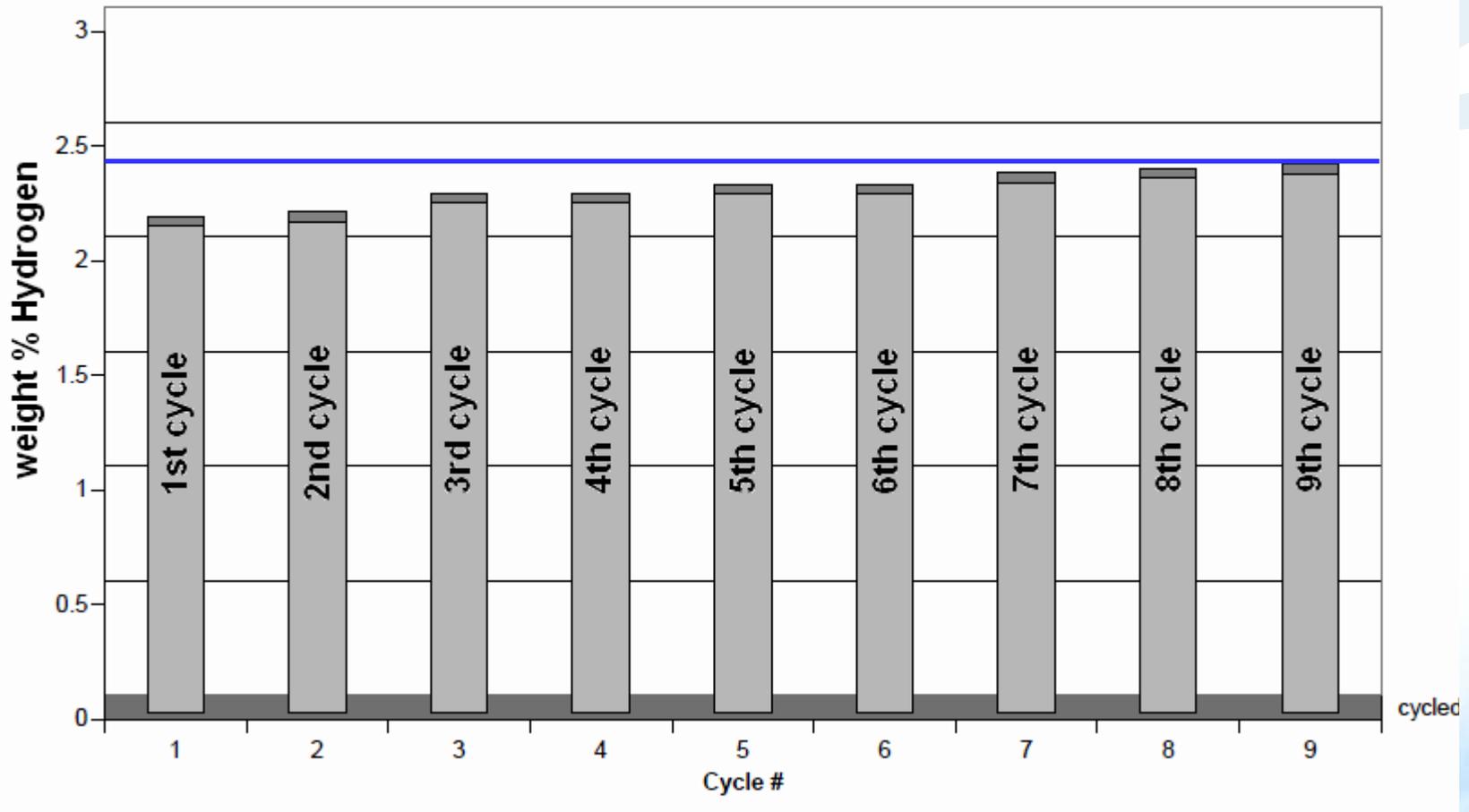
Cycling the Na₆-C₆₀ Material



Powder X-ray diffraction data of the Na₆C₆₀ material **a)** as it is first formed, **b)** after hydrogen absorption, and **c)** after hydrogen desorption. Note that the appearance of peaks unique to the absorbed material (marked with a #) and the disappearance and re-appearance of the peaks unique to the desorbed material (marked with a *) demonstrate that materials sorption reversibility

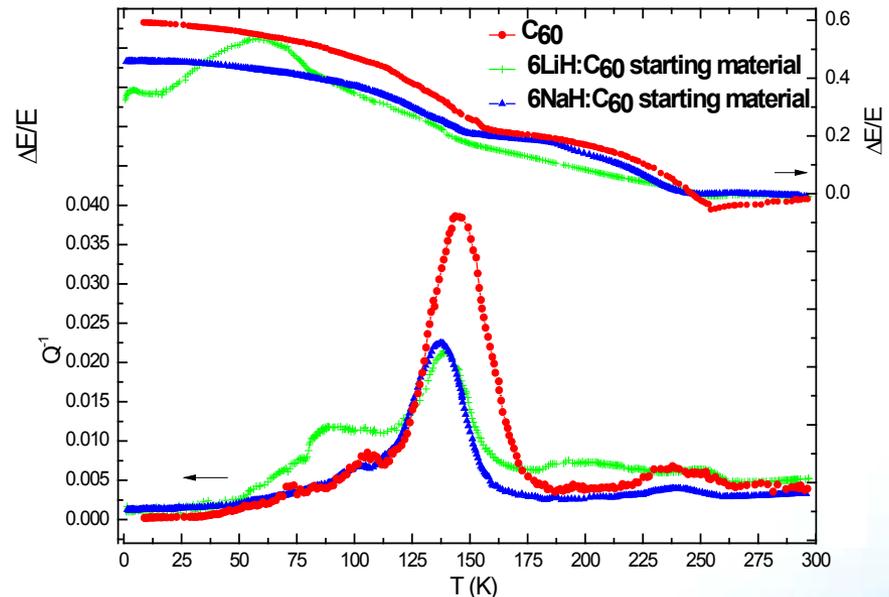
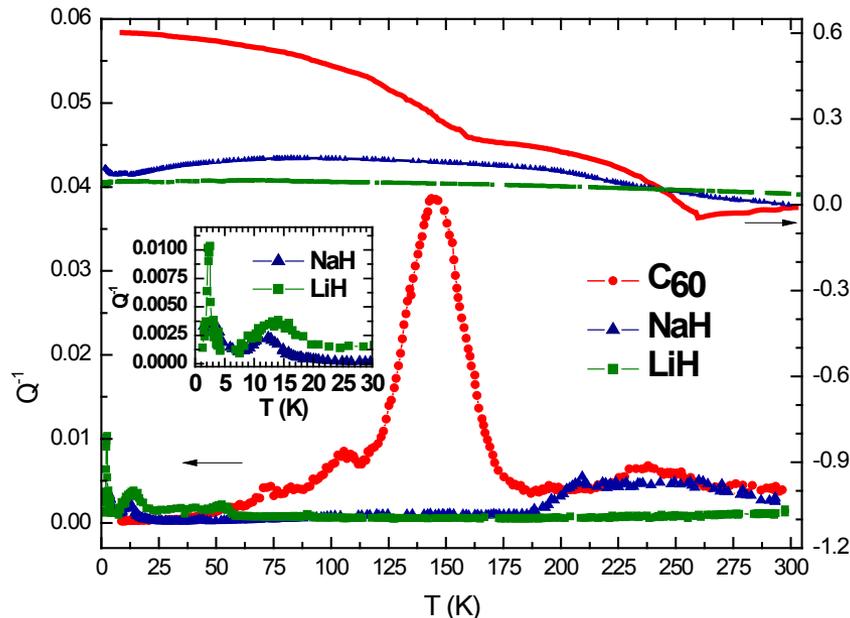
Cycling the Na₆-C₆₀ Material

The Material Retains Its Reversible Capacity Over Several Cycles (it even improves as it is cycled)



Anelastic spectroscopy measures the elastic energy loss and dynamic modulus in high vacuum in the temperature range between 1.3 and 900 K.

- 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.



Initial experiments on our as prepared materials suggest that the metal hydride (NaH, LiH) is well distributed in the material, which is attributed to our solvent-assisted mixing procedure.

Summary and Future Direction

- Simple method was developed to synthesis this unique class of materials
- The $M_x-C_{60}-H_y$ material are unique systems capable of reversible hydrogen storage at much milder conditions than $C_{60}-H_y$
- The materials are also unique in that it can store multiple hydrogen atoms per equivalent of M
- Optimum ratio of metal to C_{60} in the case of Li was identified
- Structure and phase transition due to hydrogen loading has been identified of C_{60} doped systems
- Future investigations include: Raman spectroscopy , Hydrogen/Deuterium Cycling and *in-situ* Neutron measurements and Solid-State NMR, Anelastic spectroscopy and Atomistic modeling
- Atomic scale imaging of the material, utilizing the scanning probe microscopy facility at the Center for Nanoscale Materials (CNM)

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X-ray Powder Diffraction –

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Ronnie Rutherford**

ICP-AE Elemental Analysis –

David Best

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The Center for Hydrogen Research Savannah River National Laboratory



Aiken, South Carolina

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Ragaiy Zidan

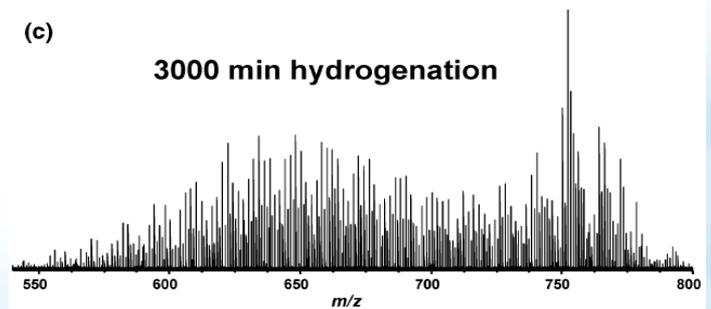
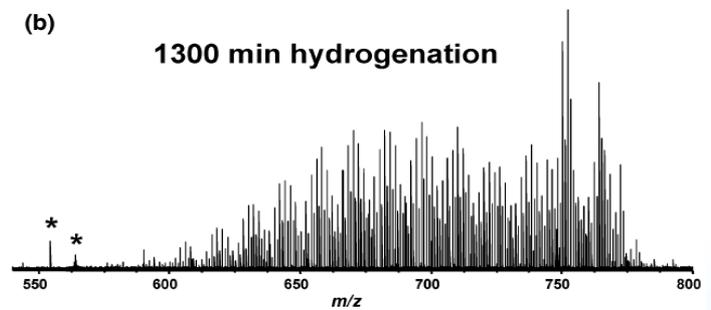
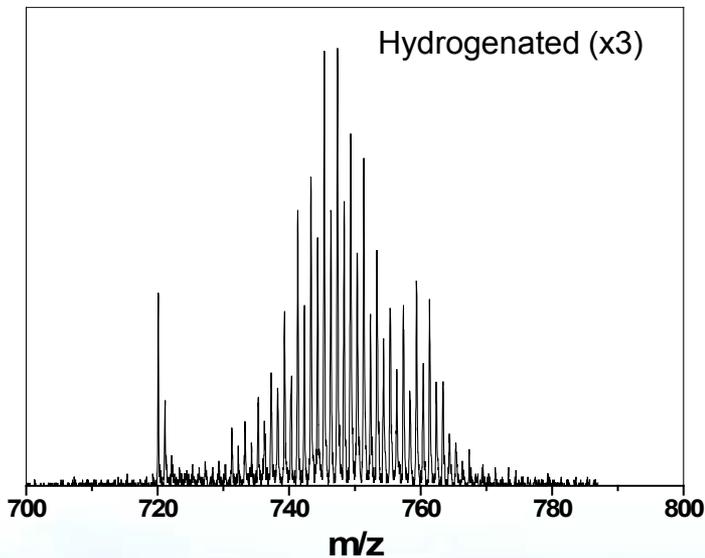
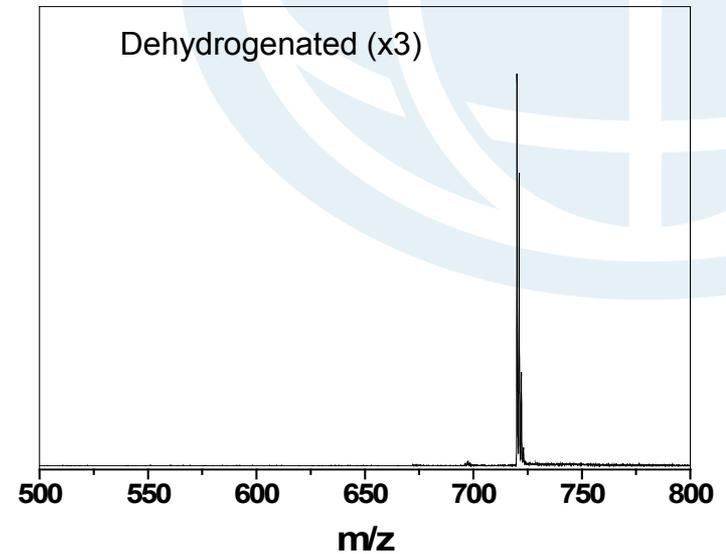
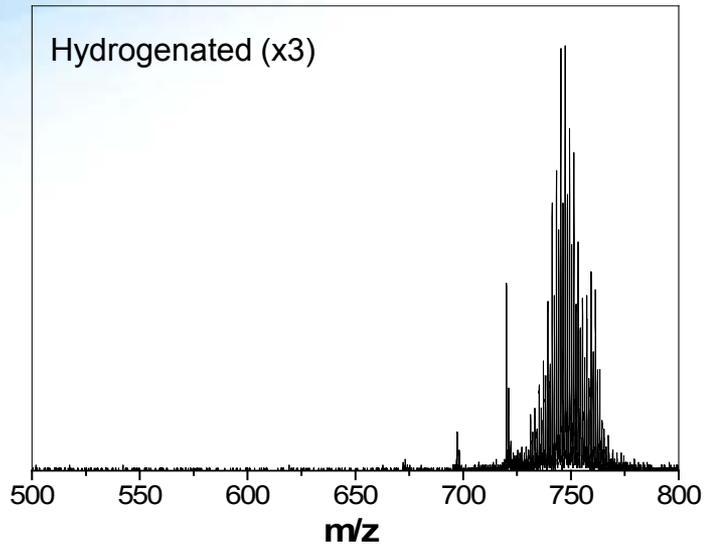
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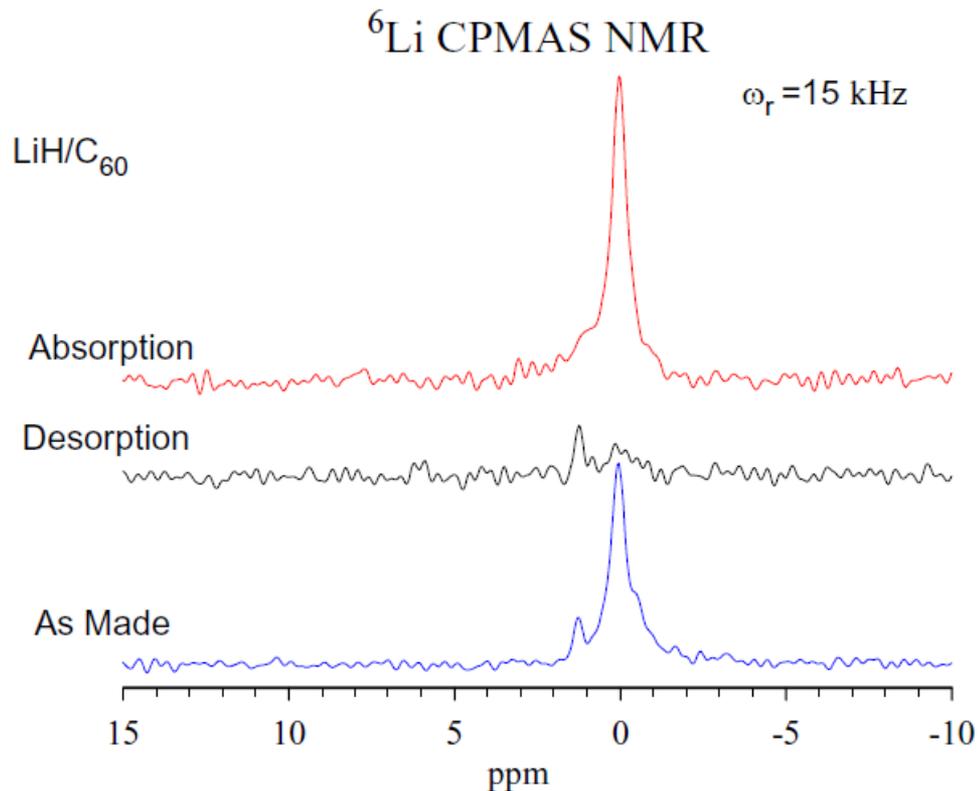
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EXTRA SLIDES

Comparison of $\text{Li}_6\text{-C}_{60}\text{-H}_{40}$ and Hydrofullerane



Cross-Polarization MAS NMR of Li-C₆₀-H_x (6:1)



Cross-polarization (CP) [Waugh *et al.*] can be used to enhance the signal of nuclei with a low gyromagnetic ratio by magnetization transfer from nuclei with a high gyromagnetic ratio (e.g. ¹H),

Absent ⁶Li peak within desorbed sample indicative of Li/H separation

In Collaboration with [Dr. Son-Jong Hwang](#), California Institute of Technology