Project ID: BES006

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

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Clean Energy Directorate

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**

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

Experimental Design:

Carbon Nanostructure

Complex Metal Hydride

mixing

Intercalation (B.M.-free)

Intercalated Material

(hydrogenated)

(desorption)

$- H_2$

$+ H_2$

(absorption)

Intercalated Material

(dehydrogenated)

Hydrogen capacity?
Reversibility?
Mechanism?

Background

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

$NaAlH_4$ and Carbon Nanostructures

Sodium Aluminum Hydride ($NaAlH_4$)

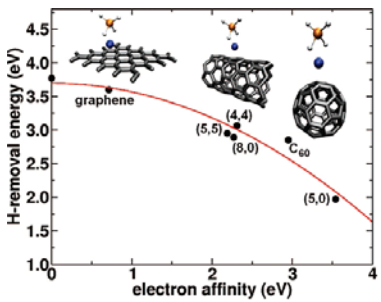
Step 1: $3\ NaAlH_4 \rightarrow 3Na_3AlH_6 + 2Al + 3H_2$ [3.7 wt%]
Step 2: $2Na_3AlH_6 \rightarrow 6NaH + 2Al + 3H_2$ [1.8 wt%]

Experimental Results

- Nanocomposites of $NaAlH_4$ with various carbon sources (graphite, CNT, and C_{60}) were synthesized by a ball-mill free procedure
- Cycling experiments of the composites (abs/des) showed that C_{60} was superior to other carbon sources tested
- C_{60} also lowered the desorption temperature of $NaAlH_4$ 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



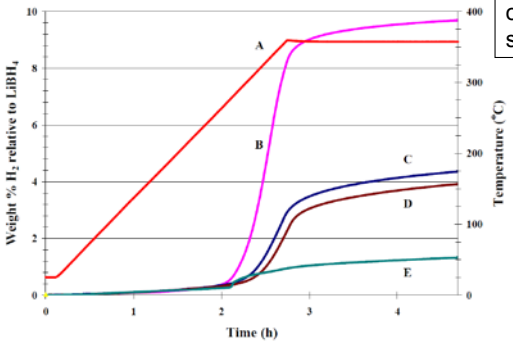
Increase in electron affinity decreases the H-removal energy (inductive effect)

$LiBH_4$-C_{60} Nanocomposite

Lithium Borohydride ($LiBH_4$)

$2LiBH_4 \rightarrow 2LiH + 2B + 3H_2$ [13.8 wt%]

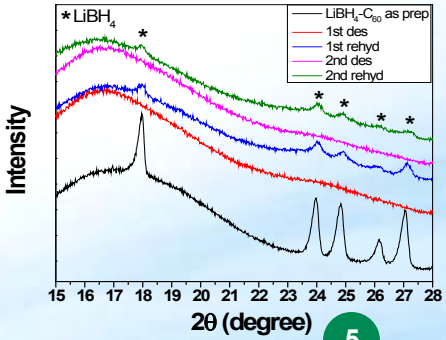
- Reversible hydrogen storage has been demonstrated by ball-milling $LiBH_4$ with MgH_2 and $TiCl_3$
- Reversible hydrogen storage has also been observed for $LiBH_4$ with nanoporous carbon scaffolds, activated carbon, and SWNT's



(**A**) T ramp (2°C/min); $LiBH_4$:C_{60} (1.6 mol%); (**B**) 1st desorption; (**C**) 2nd desorption; (**D**) 3rd Desorption; (**E**) $LiBH_4$ standard

Nanocomposites of $LiBH_4$ with C_{60} demonstrates increased desorption kinetics and reversible rehydriding (4.2 wt% H_2)

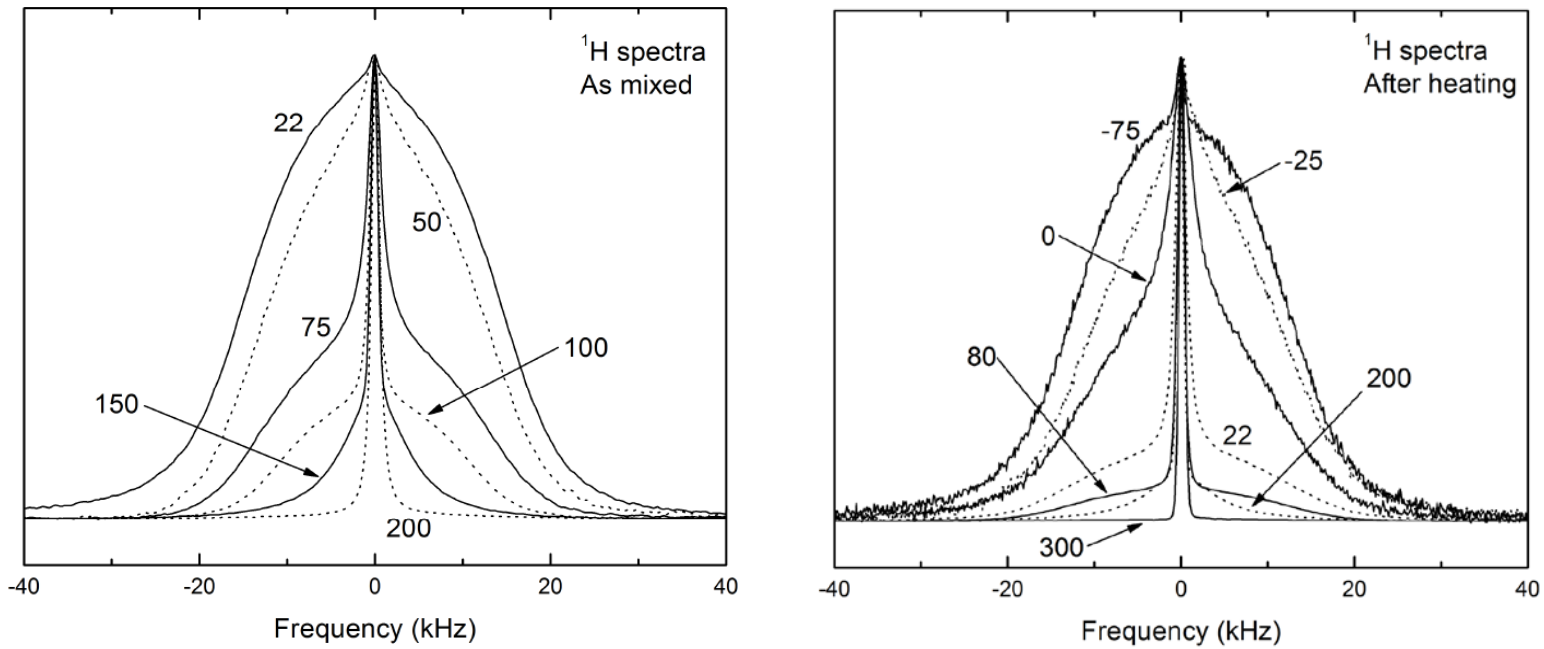
XRD confirms the reversible formation of $LiBH_4$ in the nanocomposite over multiple cycles



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*.

Effect of C_{60} on Hydrogen Mobility in $LiBH_4$

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



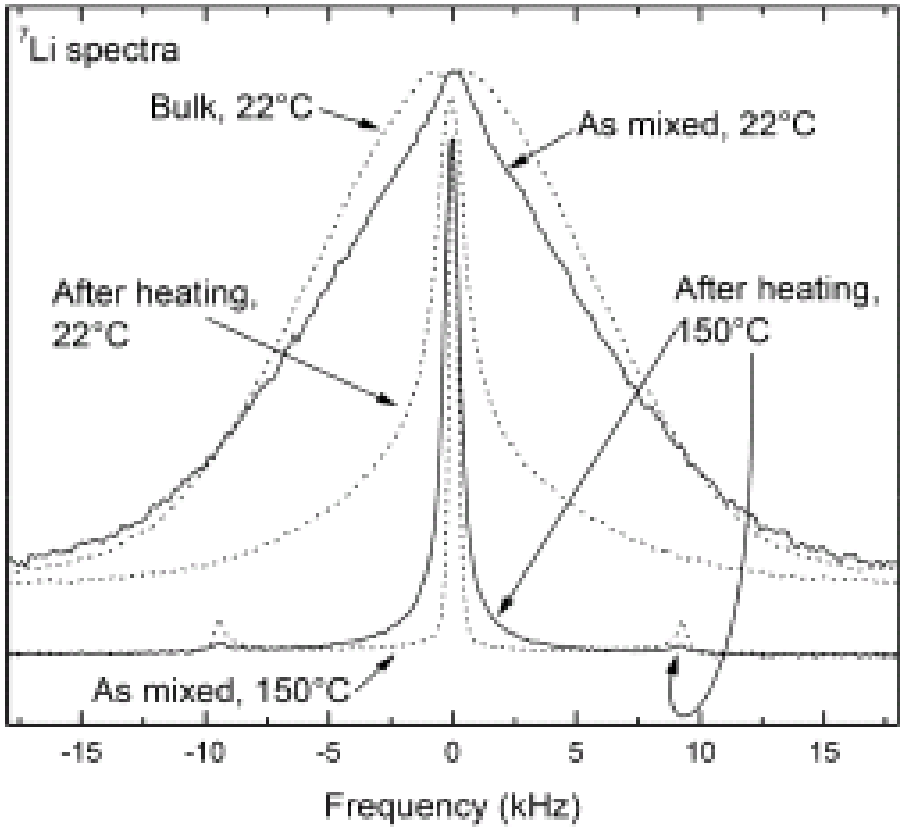
- Heating $LiBH_4$-C_{60} increases the fraction of mobile hydrogen (as BH_4^-) as well as lithium ions in the nanocomposite material
- After heating, ^{1}H spectra is similar to a $LiBH_4$ impregnated aerogel that was reported by Conradi *et al.*
  - *The fraction of mobile BH_4^- at 22°C in the $LiBH_4$-C_{60}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

Shane D. T., Corey R. L., Rayhe L. H. Wellons M, Teprovich J. A, Zidan R., Hwang S.J., Bowman R. C., and Conradi M. S., *J. Phys. Chem. C 2010, 114, 19862–19866*

Effect of C_{60} on Lithium Mobility in $LiBH_4$

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



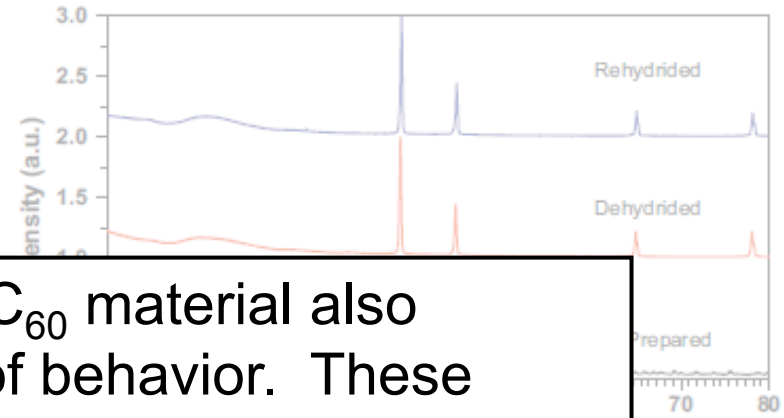
In Collaboration with Prof. Mark S. Conradi, Washington Univ. in St. Louis

Shane D. T., Corey R. L., Rayhe L. H. Wellons M, Teprovich J. A, Zidan R., Hwang S.J., Bowman R. C., and Conradi M. S., *J. Phys. Chem. C 2010, 114, 19862–19866*

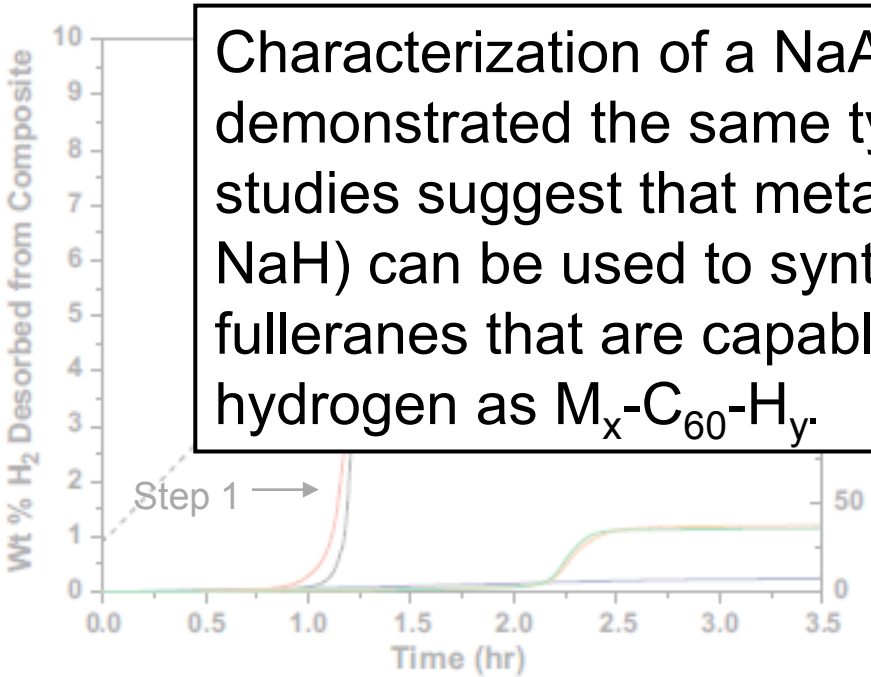
$LiAlH_4$-C_{60}

Lithium Aluminum Hydride ($LiAlH_4$)

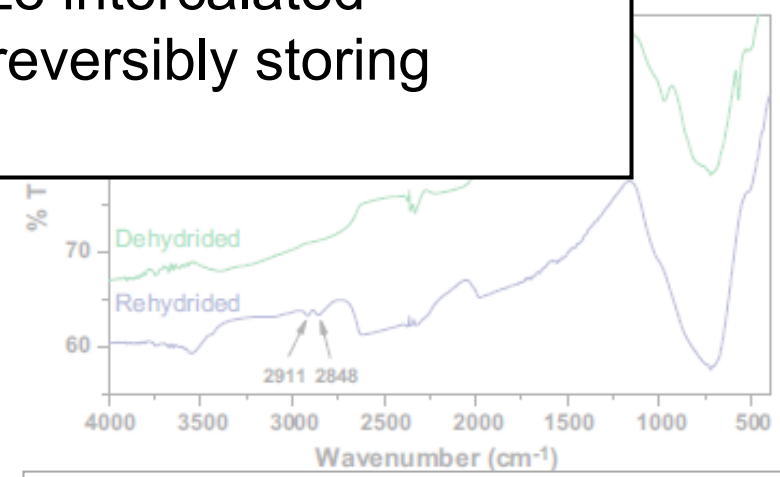
Step 1: $3LiAlH_4 \rightarrow Li_3AlH_6 + 2Al + 3H_2$ [5.3 wt%]
Step 2: $Li_3AlH_6 \rightarrow 3LiH + Al + 3/2H_2$ [7.9 wt% total]
Step 3: $LiH \rightarrow Li + 1/2H_2$ [10.5 wt% total]



Characterization of a $NaAlH_4$-C_{60} 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-C_{60}-H_y.



Rehydrogenation at 350 C and 100 bar H_2 for 11 hours
$LiAlH_4$ standard (black) , 2nd desorption (blue),
$LiAlH_4$:C_{60} (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-C_{60}-H_y.*

Teprovich, Jr., J.A.; Knight D.A.; Wellons, M.S.; Zidan, R. *J. Alloys Compd.*, **2011**, *509S*, S562-S566.

Optimization and the Formation of New materials
Case of Li_6-C_{60}-H_{40}

NANO LETTERS
Letter
pubs.acs.org/NanoLett

Synthesis and Characterization of a Lithium-Doped Fullerane (Li_x-C_{60}-H_y) for Reversible Hydrogen Storage

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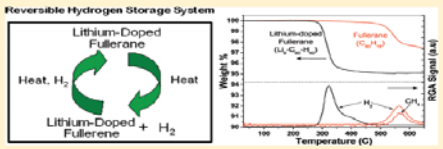
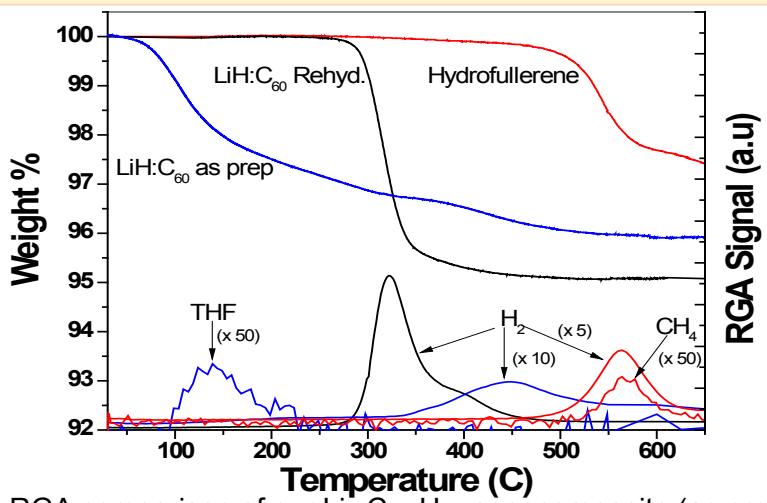
[‡]Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125, United States
[§]Department of Chemistry, University of Tennessee, Knoxville, Tennessee 37996, United States

Supporting Information

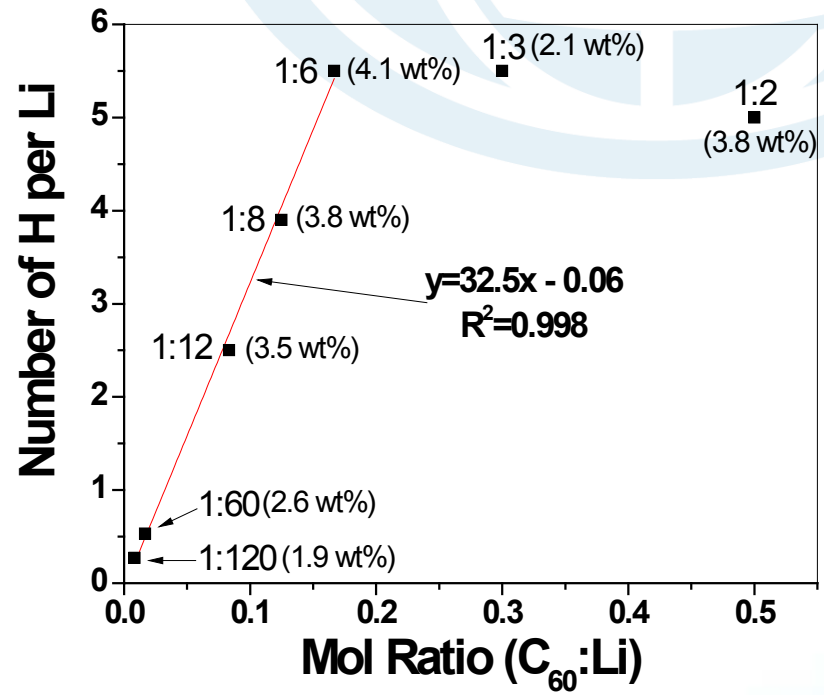
ABSTRACT: Herein, we present a lithium-doped fullerane (Li_x-C_{60}-H_y) that is capable of reversibly storing hydrogen through chemisorption at elevated temperatures and pressures. This system is unique in that hydrogen is closely associated with lithium and carbon upon rehydrogenation of the material and that the weight percent of H_2 stored in the material is intimately linked to the stoichiometric ratio of Li:C_{60} in the material. Characterization of the material (IR, Raman, UV−vis, XRD, LDI-TOF-MS, and NMR) indicates that a lithium-doped fullerane is formed upon rehydrogenation in which the active hydrogen storage material is similar to a hydrogenated fullerene. Under optimized conditions, a lithium-doped fullerane with a Li:C_{60} mole ratio of 6:1 can reversibly desorb up to 5 wt % H_2 with an onset temperature of ~270 °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 Li_x-C_{60}-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 Li_6-C_{60}-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

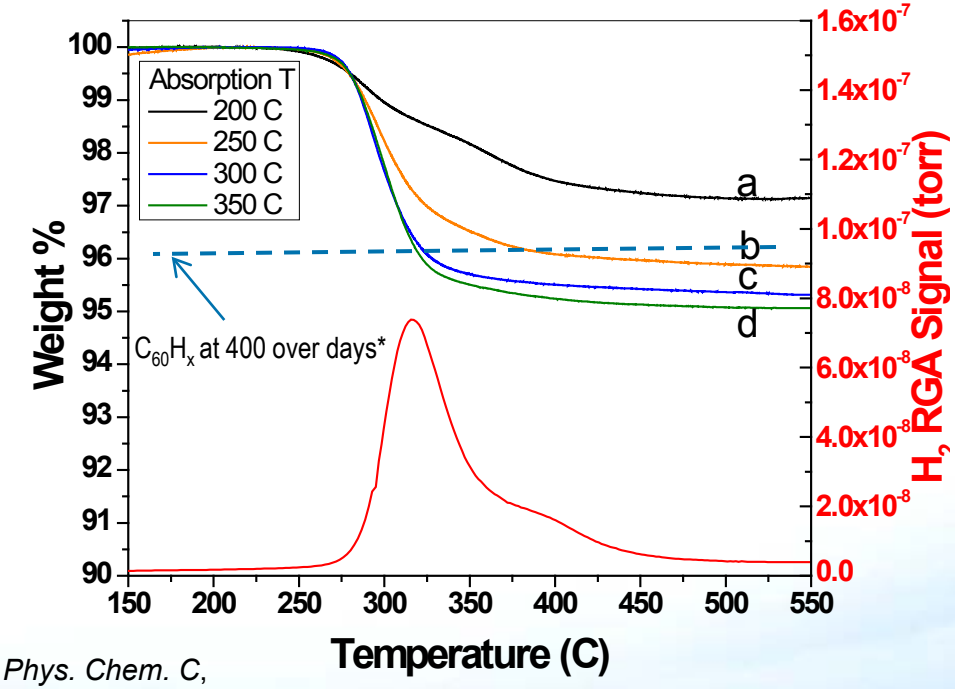


Optimization of the C_{60}:Li ratio for hydrogen storage. Samples were hydrogenated under 105 bar H_2 at 250 °C for 11 hr

Nano Letters, **2012**, *12*, 582-589.

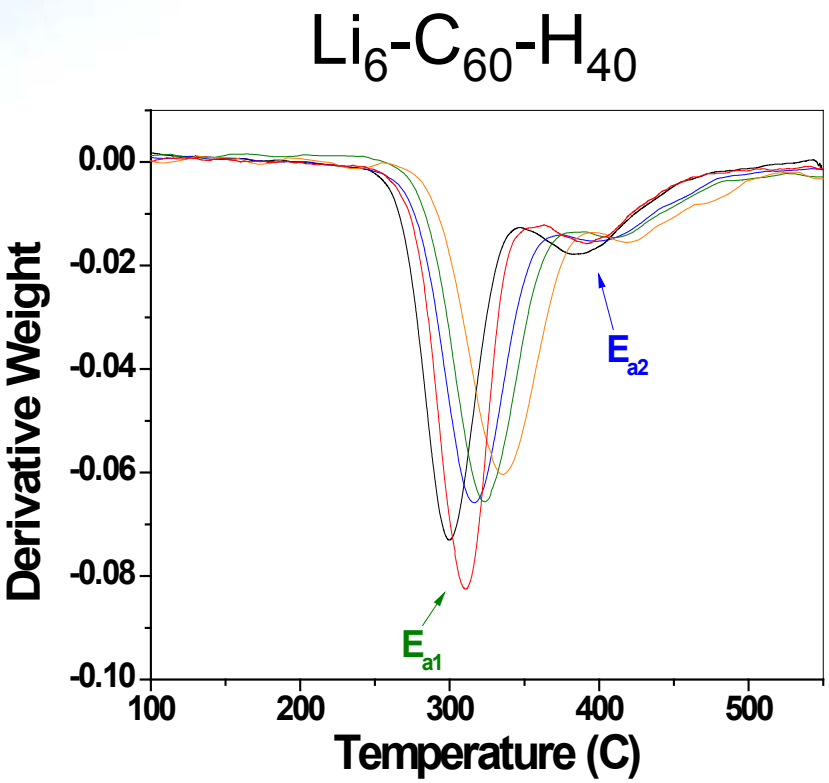
Effect of T and P on the H_2 Capacity of the 6:1 Ratio

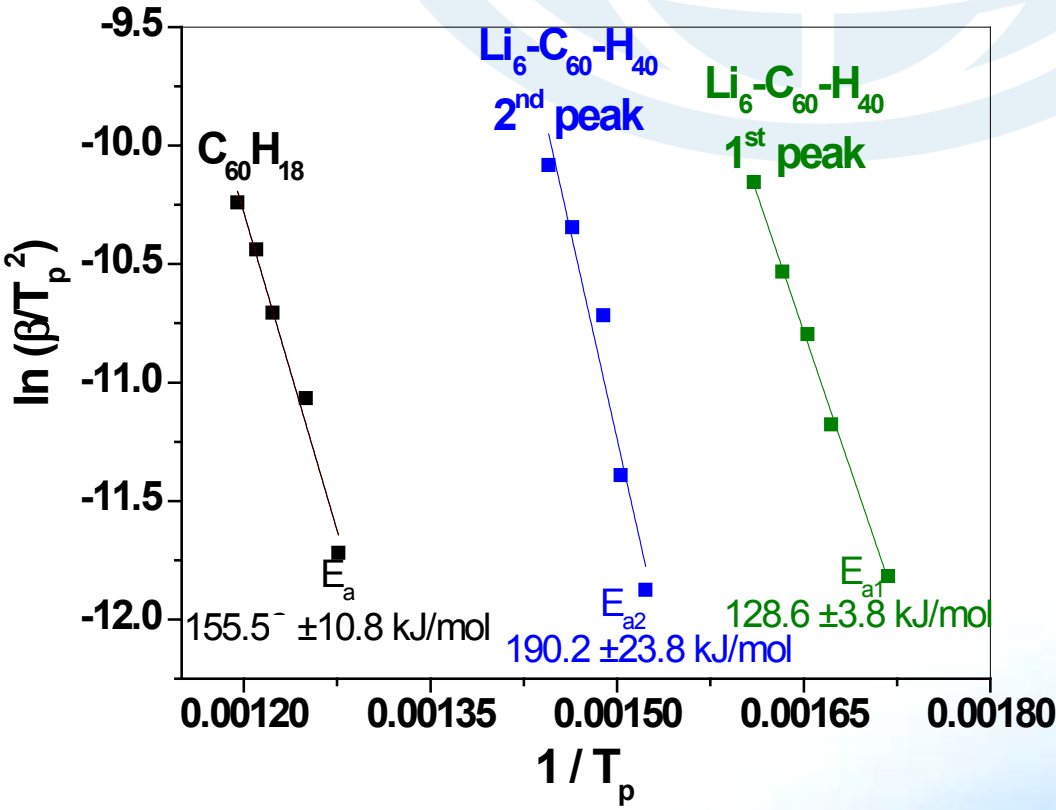
Rehydrogenation Pressure (bar H_2)	Rehydrogenation Temp. (C)	Observed H_2 wt %[a]	Ave. Value of y for Li_6-C_{60}-H_y[b]
25	350	1.8	14
50	350	2.9	23
75	350	4.1	33
105	200	2.8	22
105	250	4.1	33
105	300	4.6	37
105	350	5.0	40



* S. M. Luzan, Y. O. Tsybin, and A. V. Talyzin *J. Phys. Chem. C*, **2011**, *115*, 11484–11492

Activation Energy (Kissinger Plot)

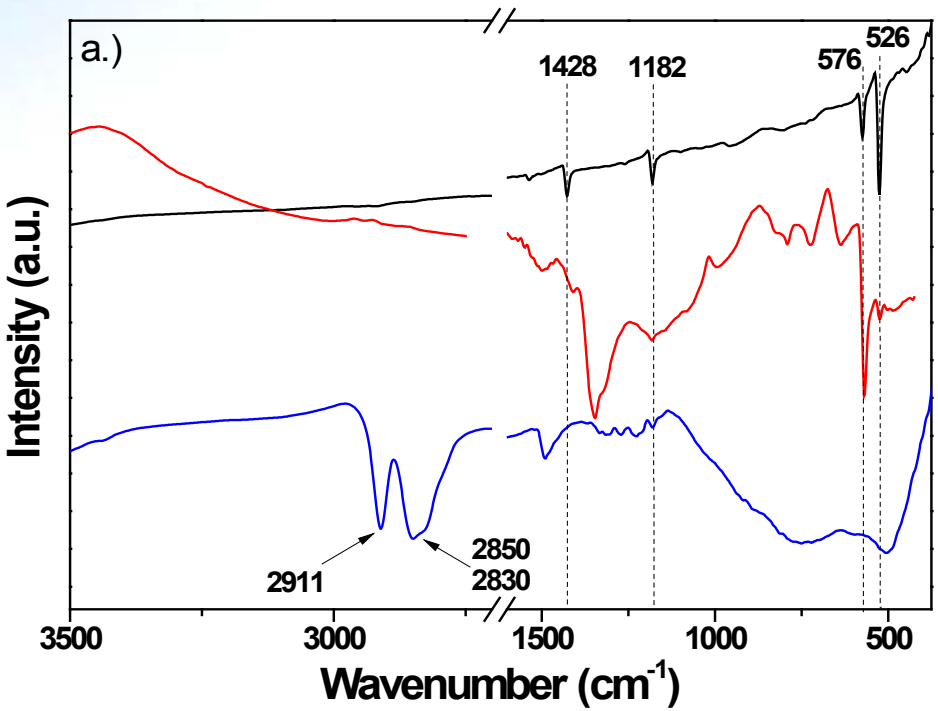


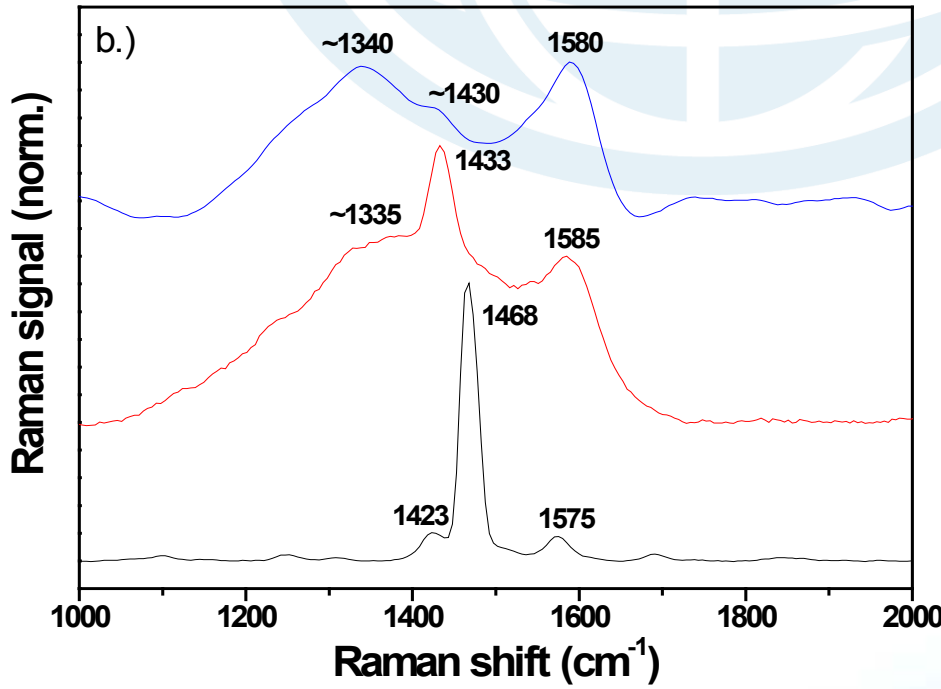


Reduction in the activation energy for the onset of H_2 desorption is lowered by 26.9 kJ/mol upon the intercalation of lithium.

IR and Raman (Where is the Hydrogen?)

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

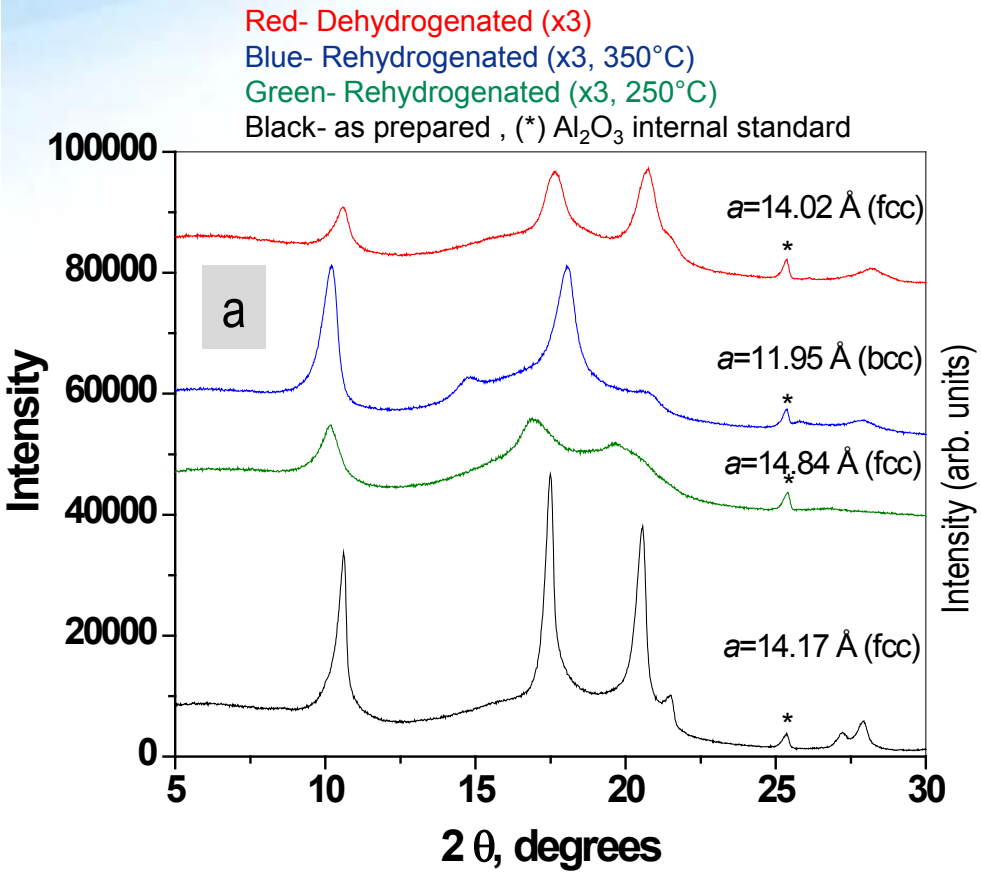


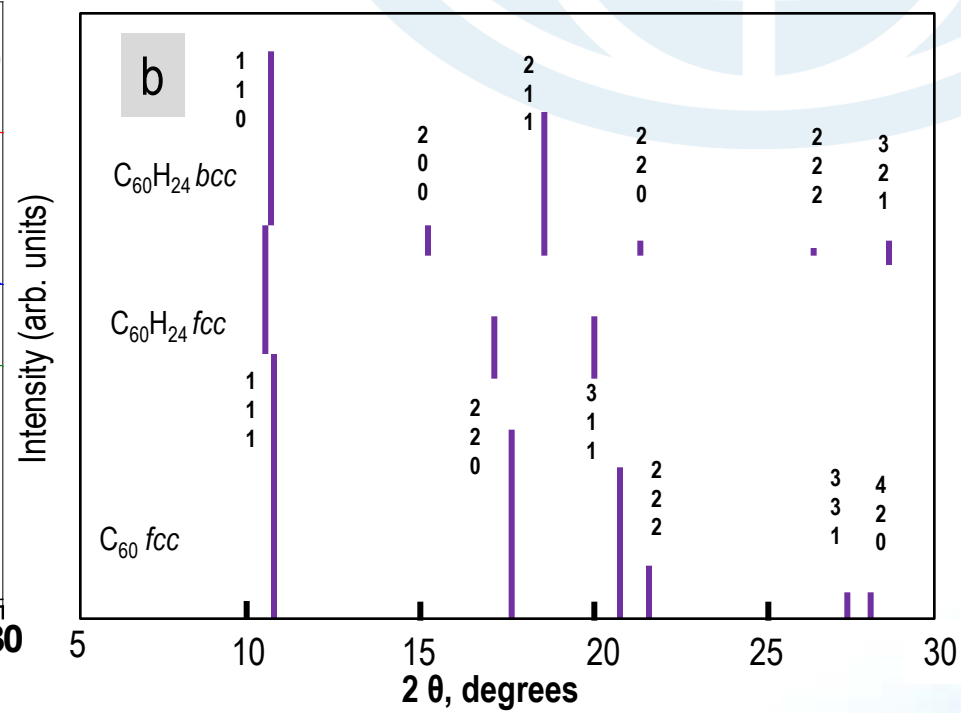


- Formation of C-H bonds is confirmed by the presence of the 3 peaks that form between 2800-3000 cm^{-1}.
- The C=C stretching vibration (1428 cm^{-1}) is shifted to ~1344 cm^{-1} and is sensitive to the degree of charge transfer to the C_{60} as well as to polymerization. (i.e. K_6C_{60} – 1341 cm^{-1} and photopolymerized C_{60} - 1324 cm^{-1})

- Upon dehydrogenation there is a shift of the A_g mode from1468 to 1433 cm^{-1} and is consistent with a 6 electron transfer to C_{60} (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



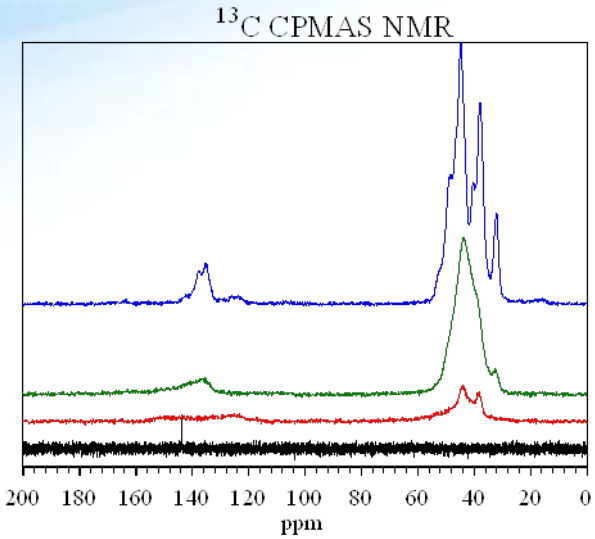


A phase reversible phase transition from *fcc* to *bcc* occurs depending on the temperature at which the hydrogenation is performed. This typically will not happen until the C_{60} is exposed to extremely high pressures (~3 GPa)

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

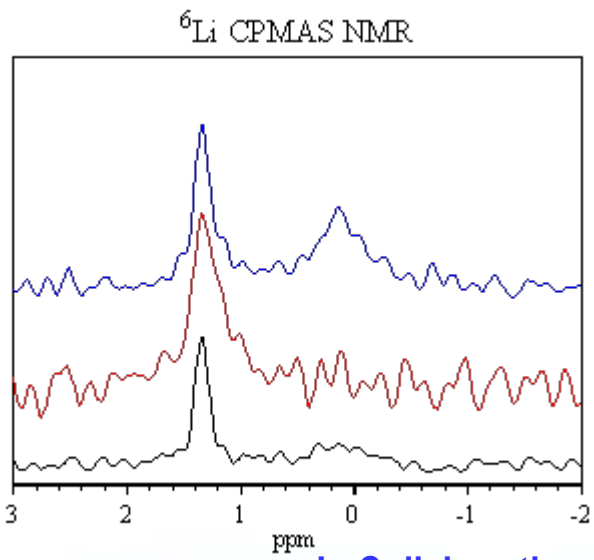
V.E. Antonova , I.O. Bashkina, S.S. Khasanova, A.P. Moravskyb, Yu.G. Morozovc, Yu.M. Shulgab,Yu.A. Ossipyan , E.G. Ponyatovsky, *Journal of Alloys and Compounds* 330–332 (**2002**) 365–368

Solid-State NMR



After the rehydrogenation, the sp^3 carbons now grew significantly and reach to about 50% for the sample rehydrogenated at 350 ºC, 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

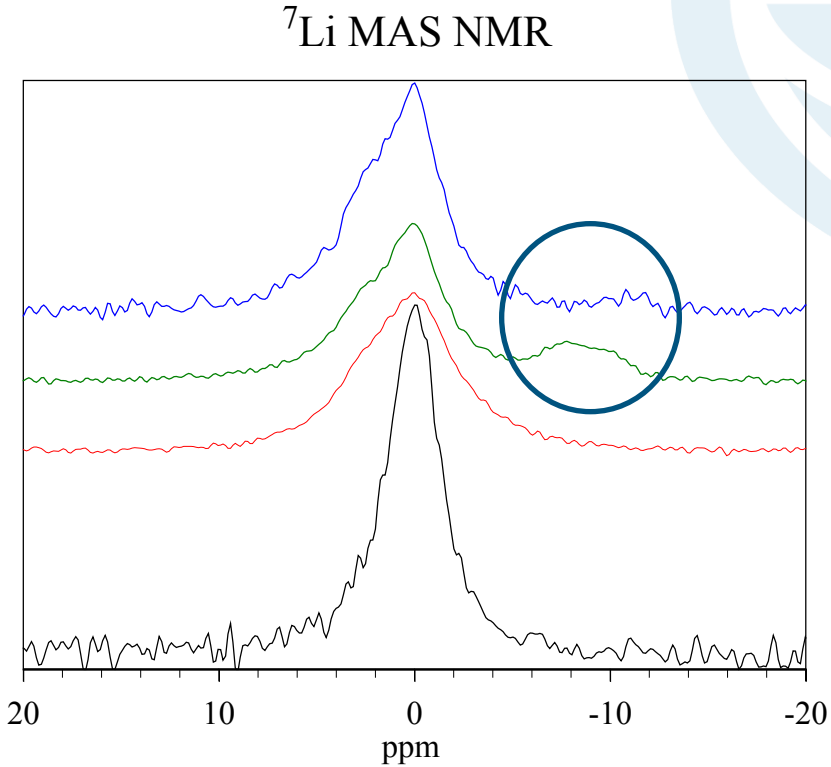


Cross-polarization (CP) [Waugh *et al.*] can be used to enhance the signal of nuclei with a low gyromagnetic ratio by magnetization transfer from nuclei with a high gyromagnetic ratio (e.g. 1H),

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

In Collaboration with Dr. Son-Jong Hwang, California Institute of Technology

Solid-State NMR



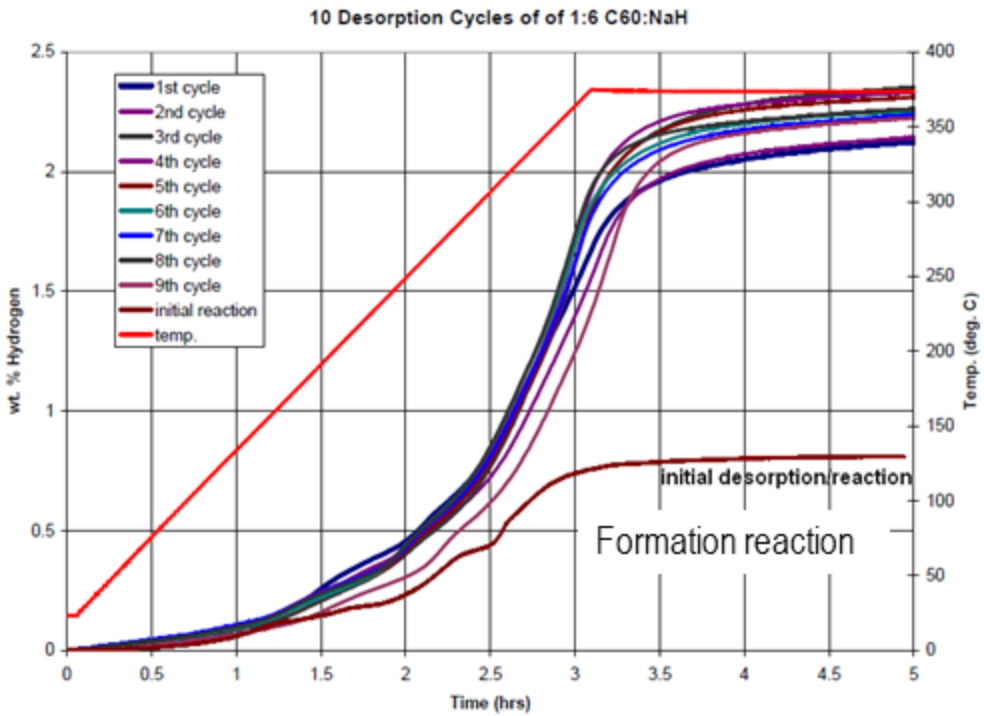
Red- Dehydrogenated (x3)
Blue- Rehydrogenated (x3, 350°C)
Green- Rehydrogenated (x3, 250°C)
Black- as prepared

Unusual far upfield shift at -9.1 and -11.5 ppm in the ^{7}Li 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 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

Na_6-C_{60} Material



Na_6C_{60}

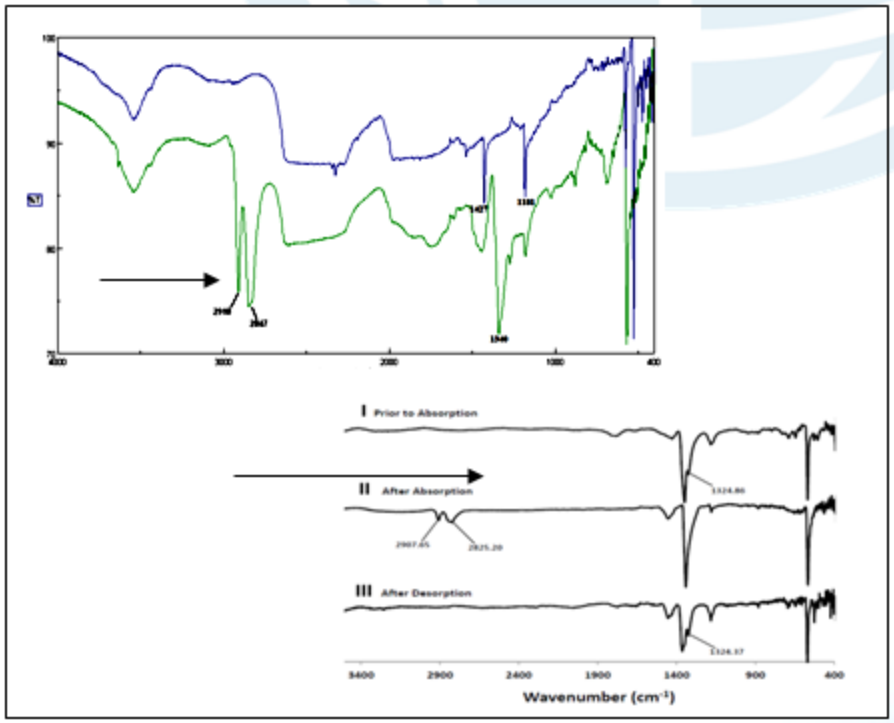
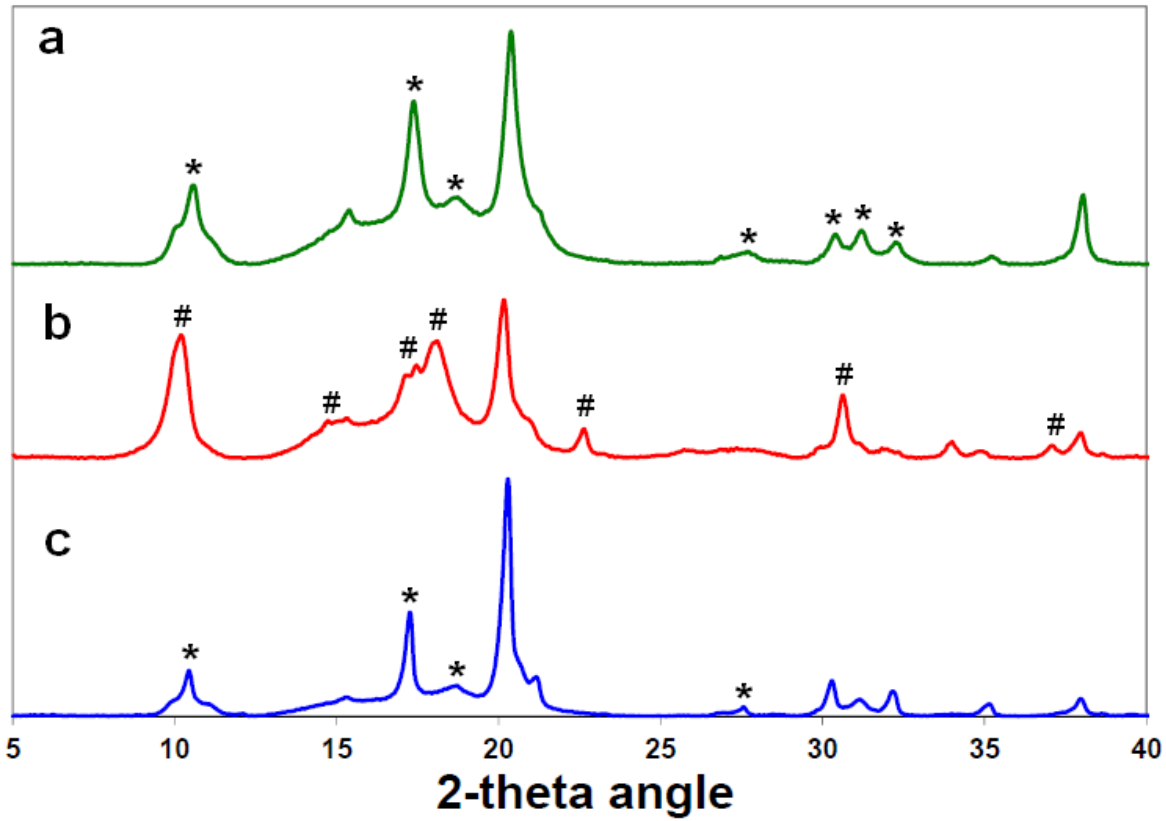


Figure shows FT-IR stack plot of the Na_6-C_{60} system. Upon rehydrogenation, the appearance of the peaks at -2907-2910 and 2825-28470 cm^{-1} indicates the formation of C-H bonds on the fullerene.

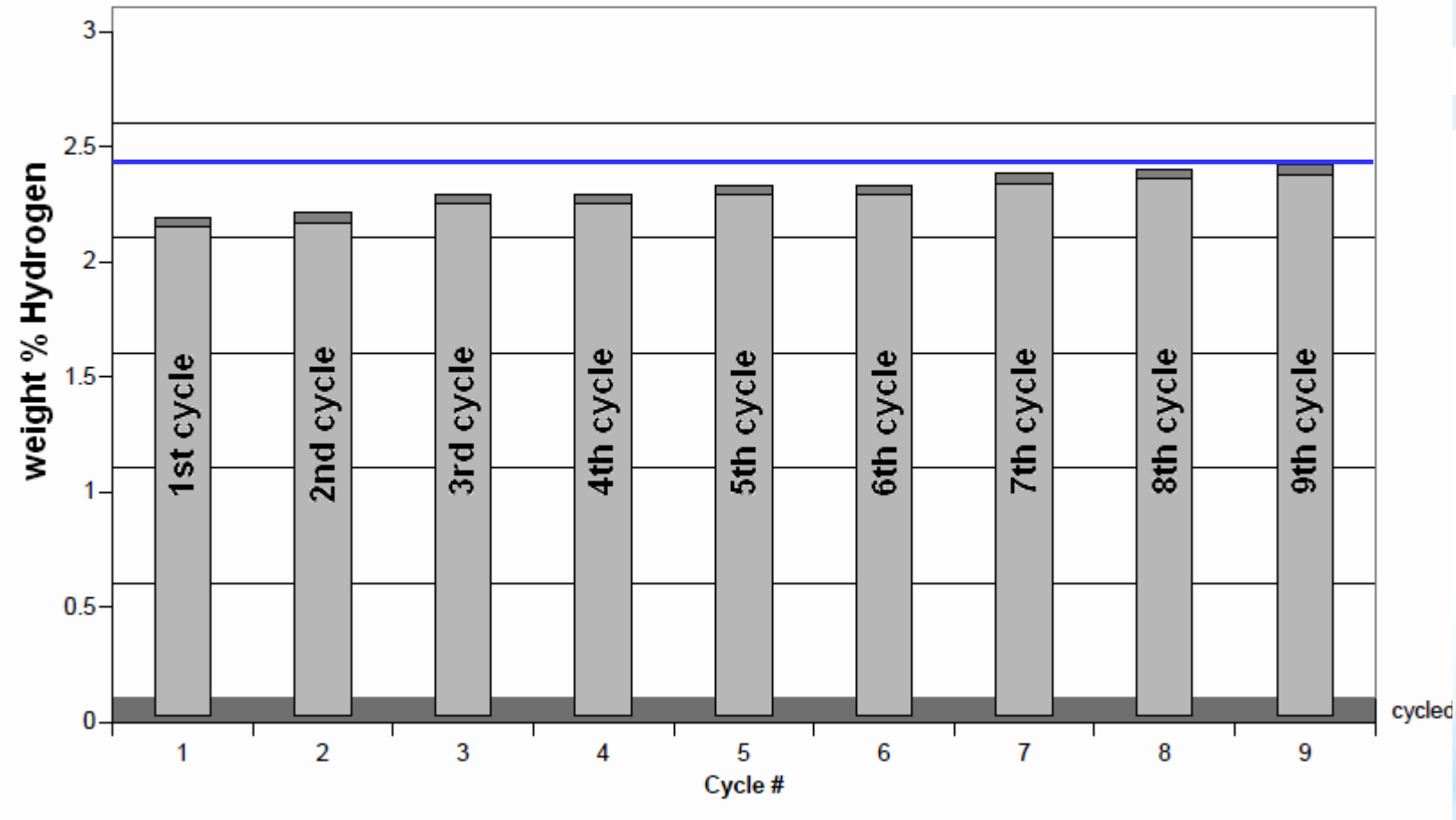
Cycling the Na_6-C_{60} Material



Powder X-ray diffraction data of the Na_6C_{60} 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-apearance of the peaks unique to the desorbed material (marked with a *) demonstrate that materials sorption reversibility

Cycling the Na_6-C_{60} Material

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

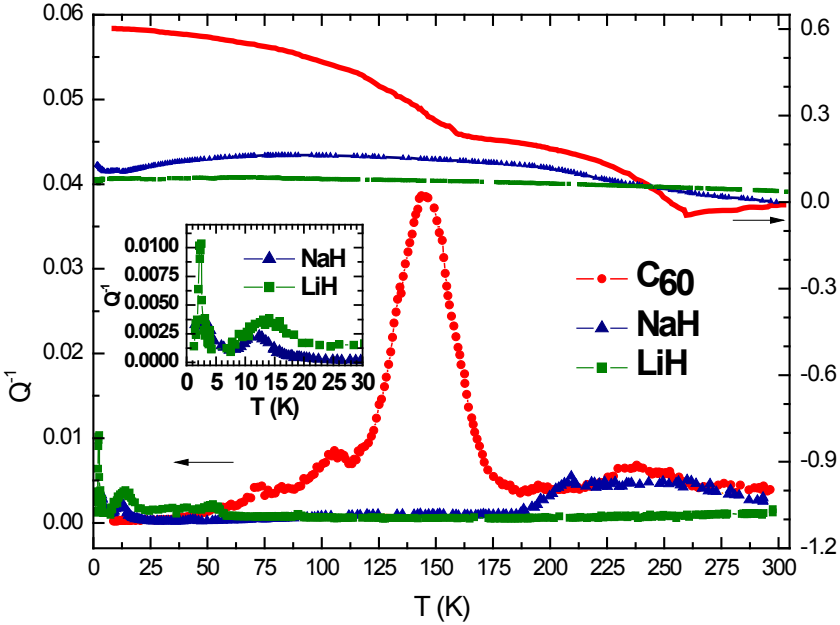


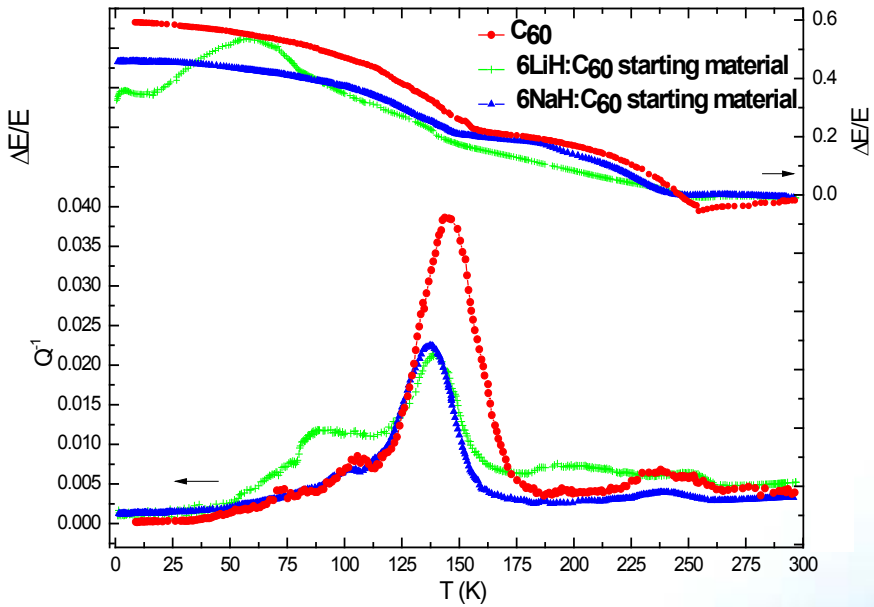
SRNL-TR-2011-00103

Ongoing Work – Anelastic Spectroscopy

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.

In Collaboration with Prof. Rosario Cantelli, Sapienza University of Rome

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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Savannah River National Laboratory

X-ray Powder Diffraction –

Patrick O'Rourke, David Missimer, Ronnie Rutherford

ICP-AE Elemental Analysis –

David Best

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END of Slides

Ragaiy Zidan

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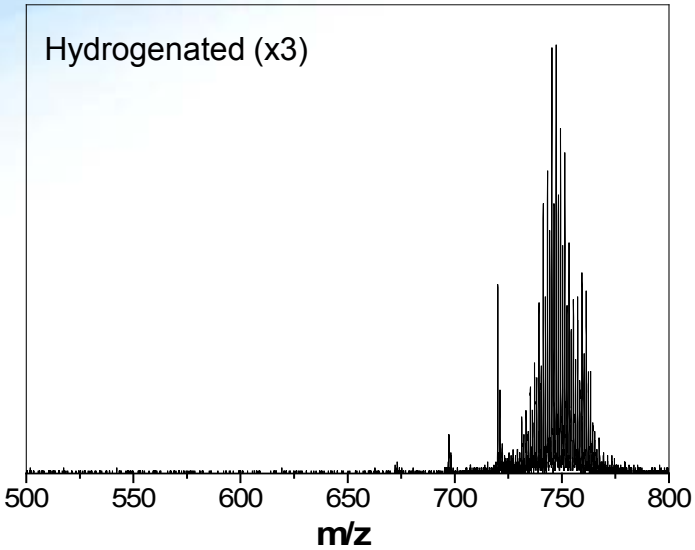
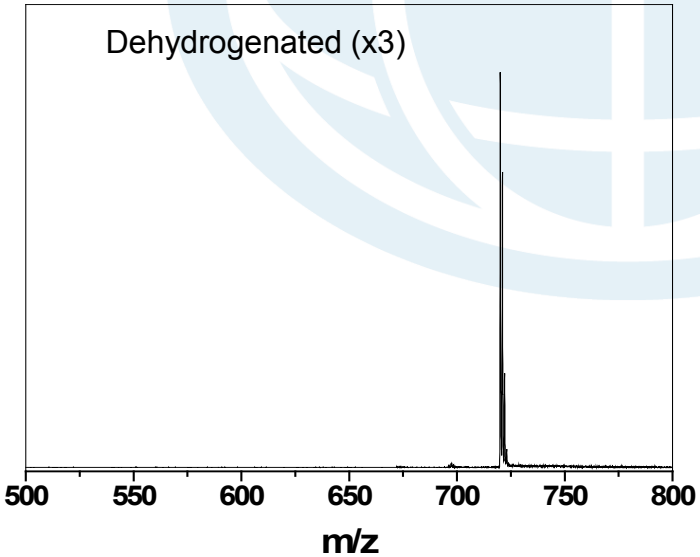
Clean Energy Directorate

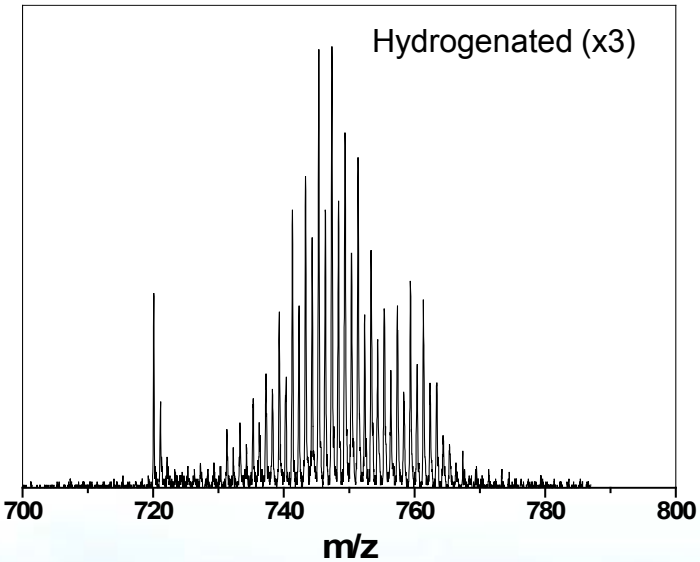
Savannah River National Laboratory

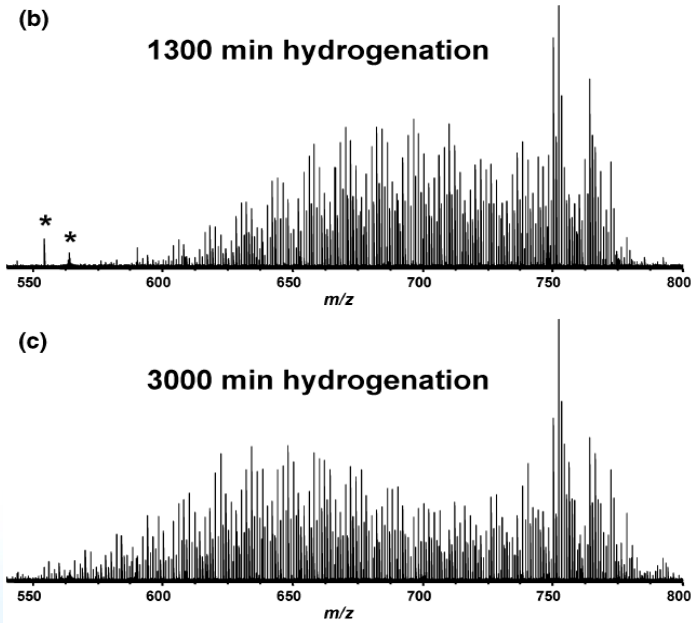
EXTRA SLIDES

Comparison of Li_6-C_{60}-H_{40} and Hydrofullerane

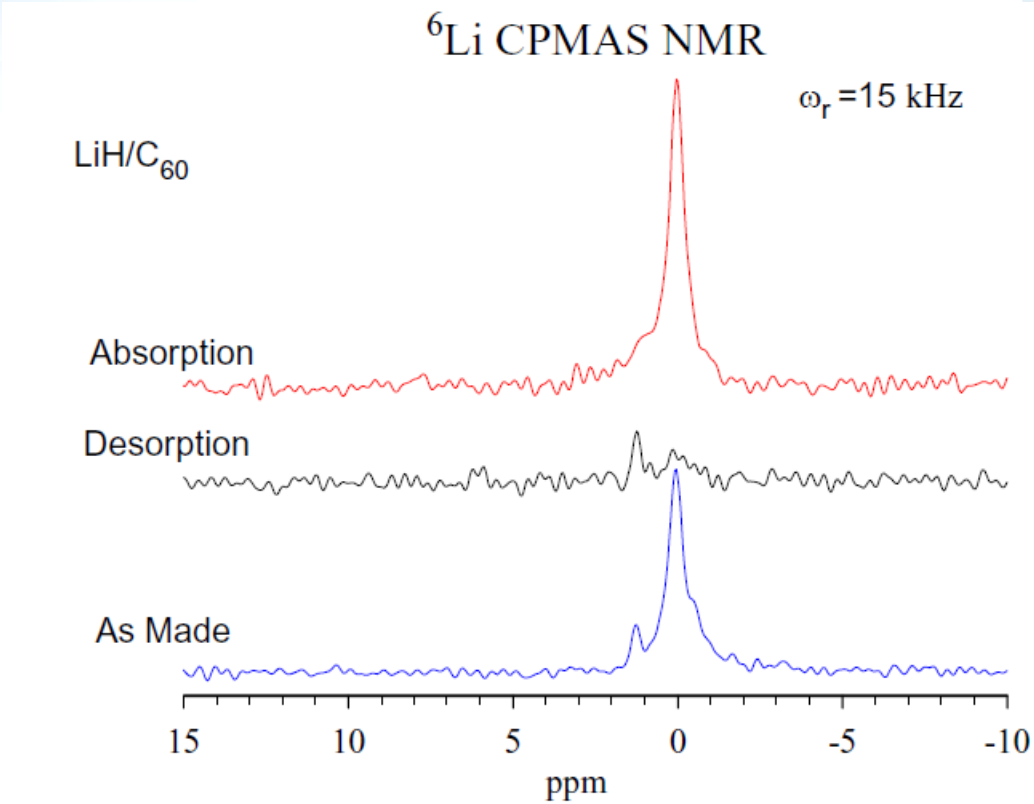








Cross-Polarization MAS NMR of Li-C_{60}-H_x (6:1)



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 ^{6}Li peak within desorbed sample indicative of Li/H separation

In Collaboration with Dr. Son-Jong Hwang, California Institute of Technology