Fundamental Studies of Surface-Functionalized Mesoporous Carbons for Thermodynamic Stabilization and Reversibility of Metal Hydrides

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University of Missouri – St. Louis

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Project ID # ST139

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Overview

Timeline and Budget

For Competitively Selected Projects:
(lab and non-lab projects)

- Project Start Date: 10/01/2016
- Project End Date: 09/30/2019
- Total Project Budget: $625,000
  - Total Recipient Share: $125,000
  - Total Federal Share: $500,000
  - Total DOE Funds Spent*: $83,333 (As of 3/31/17)
- Total DOE Funds Received to Date: $250,000 (Budget Period 1)

Barriers

- complex hydrides with low desorption enthalpies (e.g. AlH_3, $\Delta H<10$ kJ/mol) are generally too unstable for rehydriding under moderate temperatures and hydrogen overpressure
- reversible hydrogen storage using alane with volumetric and gravimetric densities of >70 g H_2/L, > 7 wt% H_2

Partners

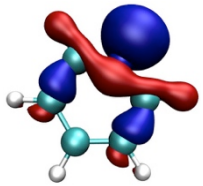
- Project Lead
  - **University of Missouri, St. Louis** (UMSL)
- Partners:
  - Washington University in St. Louis (WU), Saint Louis University (SLU)
- Collaborators:
  - SNL/CA through HyMARC, NIST

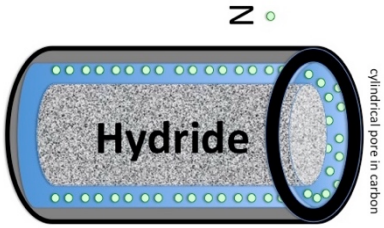
Relevance

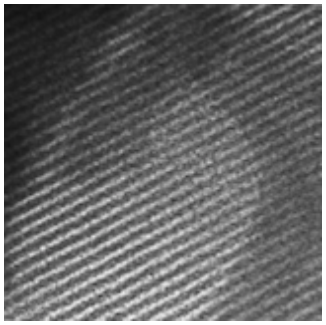
- Objectives:
  - Utilize the surface chemistry of the hydride/active-framework interactions to design functionalities that allow the use of unstable complex hydrides for hydrogen storage
  - Demonstrate Lewis acid / Lewis base interaction between Al in AlH_3 and pyridinic nitrogen (pyrN) in N-doped carbon nanoframeworks
  - Demonstrate differences between non/functionalized carbon nano-frameworks
  - Demonstrate some reversibility of AlH_3 de/re-hydriding (18 month Go/No-go)
- Impact on the <u>barriers</u> and <u>other specific targets and milestones</u>:
  - Successful completion of this project will allow the design of surface-functionalized nanoporous carbons for confinement and optimization of hydrogen storage materials and, more broadly, energy-storage materials including batteries and pseudo- and super-capacitors (see overview slide for specific targets)
  - Benefits include chemical specificity and control over compound stability, kinetics, and reactant confinement to mitigate diffusion and phase separation
  - Our project directly impacts other DOE projects where effects of nanoscale hydrides are in contact with carbon substrates

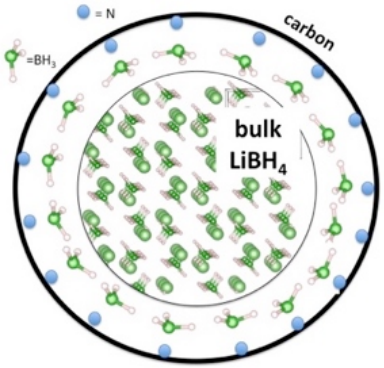
Approach

- <u>Hydrogen-storage Barriers:</u>
  - Several hydrides have enthalpies that are too low, e.g. AlH_3 (~11 kJ/mol H_2)
  - Poor reversibility with solid storage hydrides due to kinetic barriers and macroscopic phase segregation in bulk materials
- <u>Technical approach</u>:
  - High surface area carbon frameworks provide an opportunity to utilize specific surface <u>functionalization</u> for controlled chemistry and interactions of the surface with hydrides incorporated inside
  - Many mesoporous carbons have been tried before (HSAG, aerogels, carbon black, etc.) but <u>*none have been specifically functionalized*</u>
- GNG: demonstrate LA/LB complex



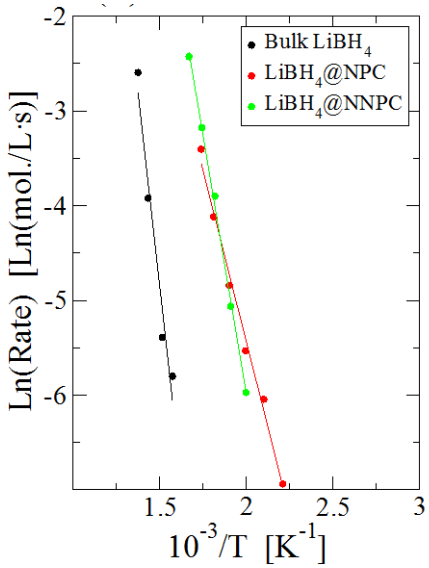


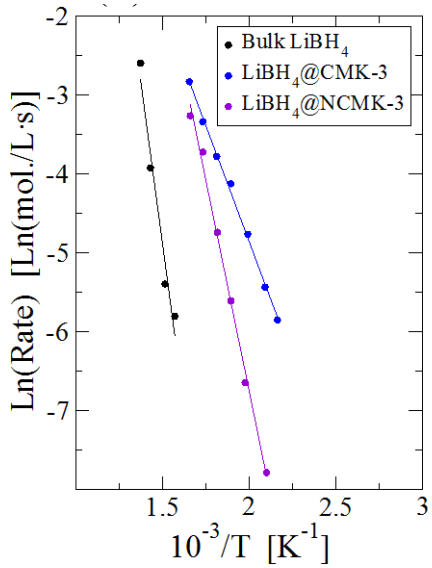


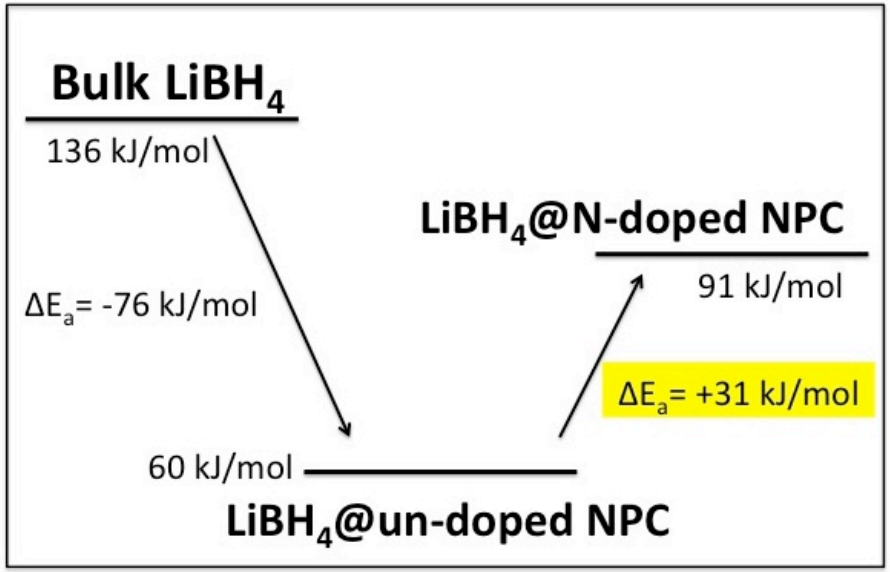


Approach

Isothermal Desorption Data Indicate Borane Interaction with Substrate Provides Stabilization in Nitrogen-doped Carbons

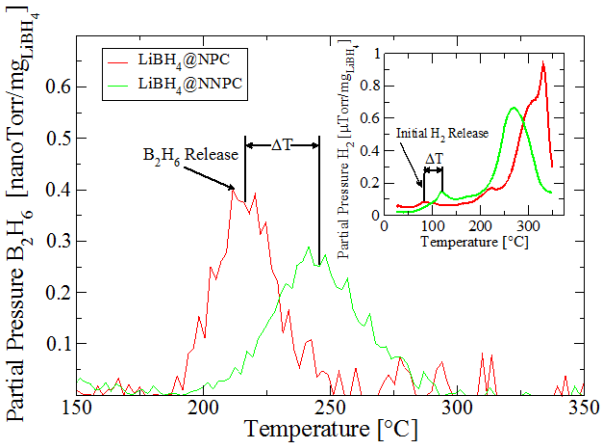






- TPD indicates B_2H_6 release at *higher* temperature in N-doped carbon
- N-doped carbons have *higher activation energy*
- Suggests borane interaction with carbon

Carr and Majzoub, JPCC, 120, 11426, 2016



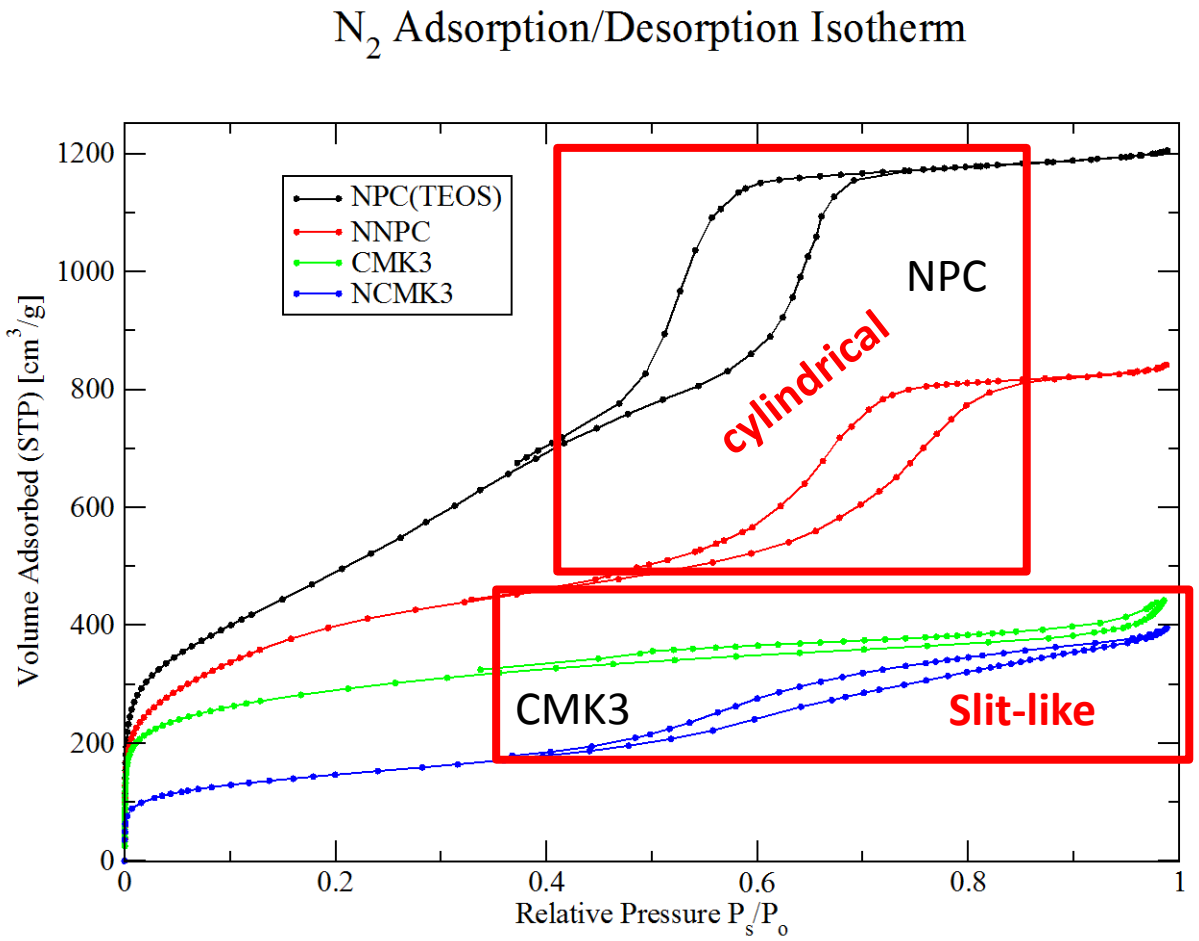
Accomplishments and Progress

N_2 Adsorption Isotherms Indicate Difference in Carbon Pore Structure

- ✓ Task 1: Subtask 1.1: Preparation of N-doped NPC. Y1Q1-Y1Q2
- ✓ Task 1: Subtask 1.2: Preparation of N-doped CMK3. Y1Q1-Y1Q2

- ✓ Task 1: Subtask 1.3 Characterization of carbons. Y1Q1-Y2Q2

Carbon prep with EDA



X-ray Photo-electron Spectroscopy Confirms Pyridinic Nitrogen in N-doped Carbons

✓ Task 1: Subtask 1.3: Characterization of N-doped carbons via XPS and porosimetry. Y1Q1-Y2Q2

Preparation of carbon with N/^{15}N

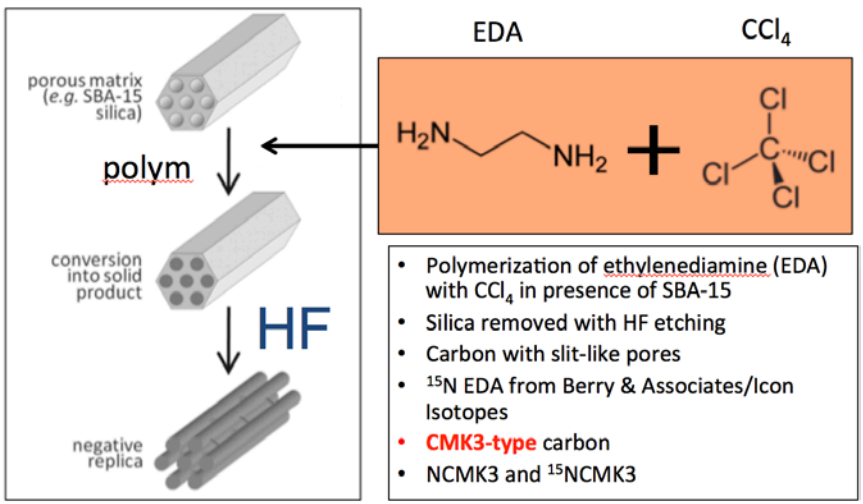
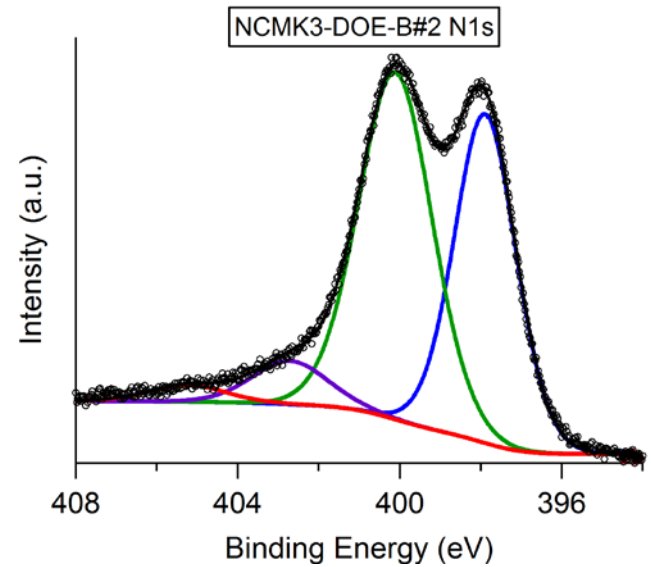


Image: Chem. Mater. **2008**, *20*, 961.



Representative XPS N 1s spectra of the sample made with EDA (NCMK3-DOE-B#2). Four different bonding environments include pyridinic (blue), pyrrolic (green), graphitic (violet) and oxidized (red). Data taken at SNL/CA.

Collaboration: SNL/CA, HyMARC

Nitrogen Content Higher in CMK3-type Carbons

Carbon Morphologies	
Bare	**Nitrogen-doped**
NPC	NNPC
CMK3	NCMK3
NPC=(bigger, open pores)	CMK3=(smaller slit-like pores)

sample	C (at.%)	O (at.%)	N (at.%)	pyridinic N (at.%)	surface area (m^2/g)	pore vol. (cc/g)
NPC	96	4	-	-	1650	1.8
NNPC	85	11	5	2	1450	1.3
CMK3	98	1	-	-	1000	0.7
NCMK3	81	6	13	5	600	0.4

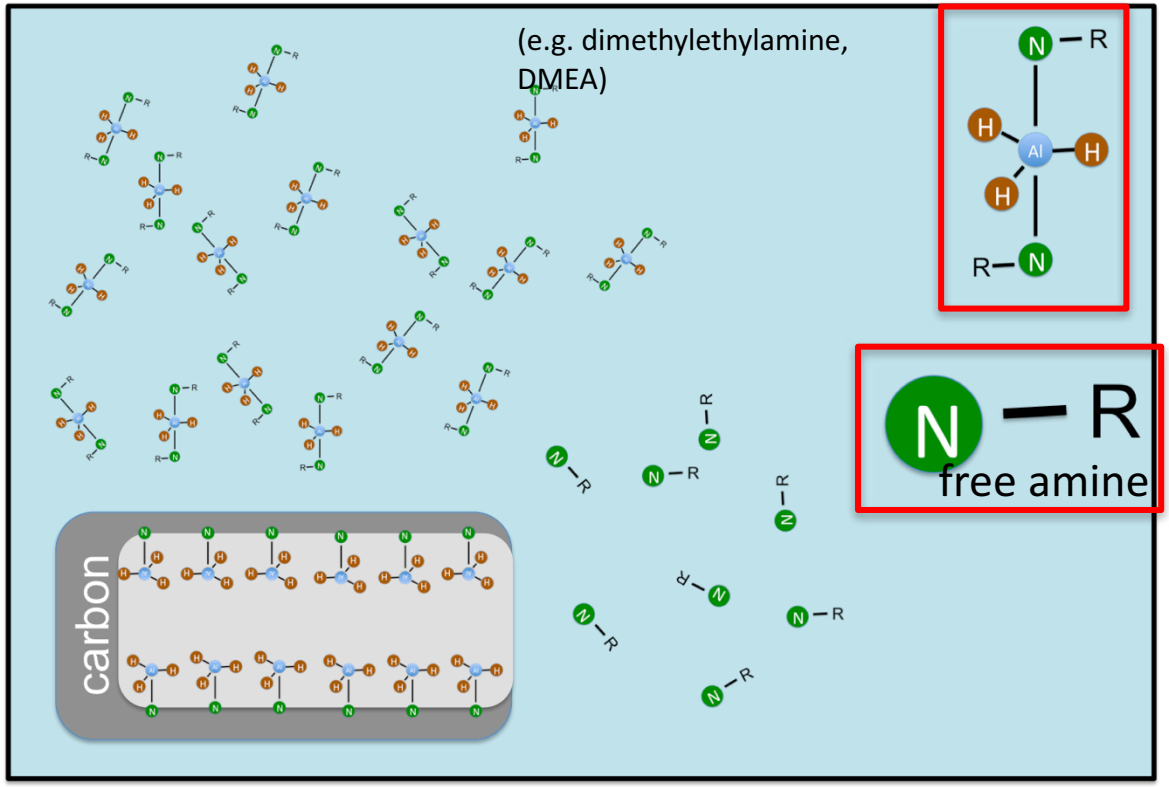
Higher N content is possible

Two Strategies for AlH_3 Incorporation Into N-doped Carbon Frameworks

1) **Infiltration with base-stabilized AlH_3**
   - **pros:** *molecular AlH_3, direct base exchange with template pyridinic N*
   - **cons:** *may be a lower level of doping, solvent and amine may remain*
2) **Infiltration with $NaAlH_4$**
   - **pros:** *much larger doping is likely, may introduce additional electron density in the framework if Na intercalates*
   - **cons:** *presence of Na complicates process*
   - Note: (1) early literature on $NaAlH_4$@carbon uses much different carbons (aerogel, HSAG, etc.) (2) Na *may* intercalate in amorphous HC, leaving AlH_3 inside the pores and Al outside the pores

Solution Infiltration / Base Exchange with DMEA-stabilized Alane

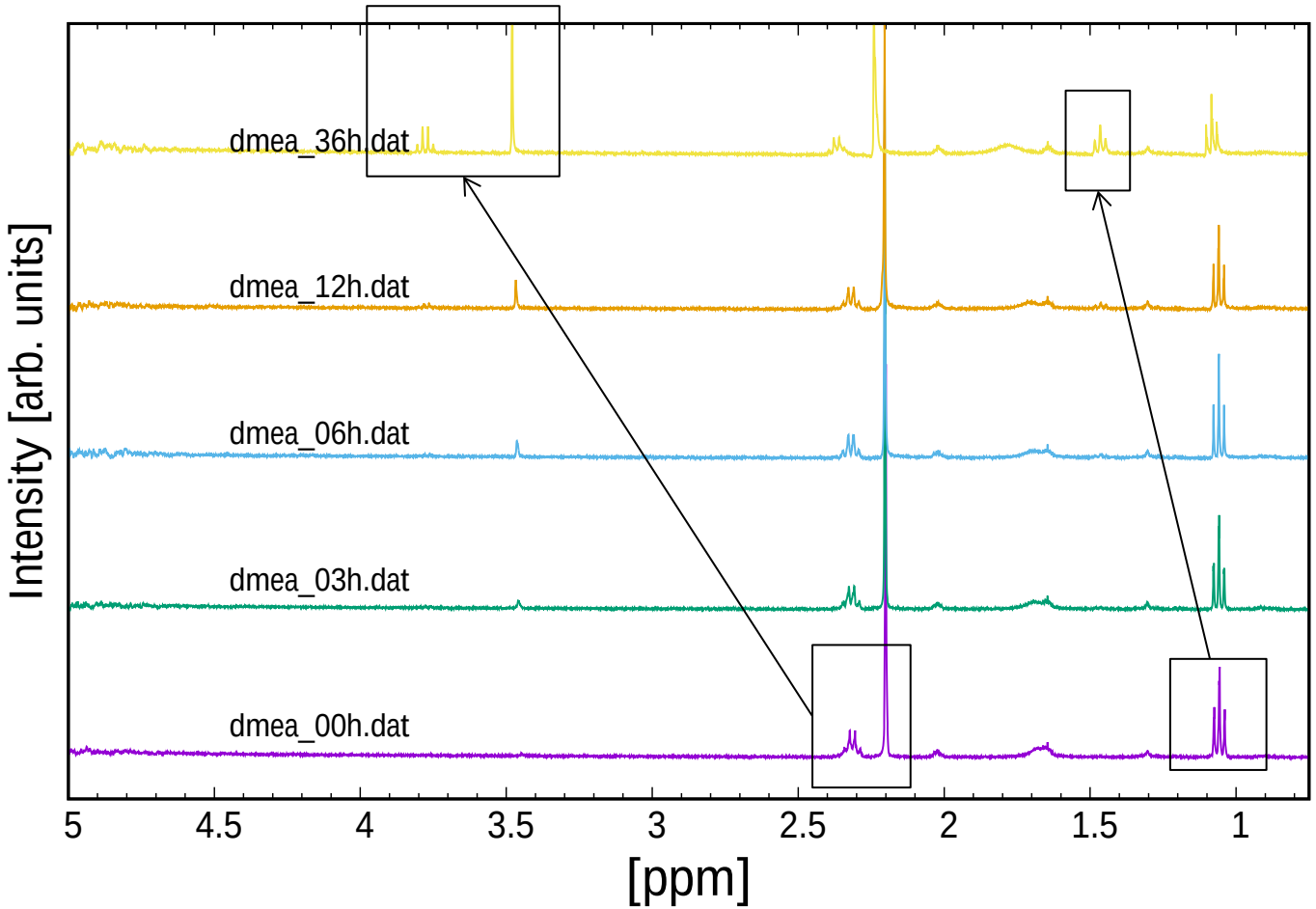
✓ Task 2: Subtask 2.2: Alane infiltration via solution-based methods including neutral tertiary amine-stabilized alanes. Y1Q3-Y2Q2



- N-doping may induce precipitation outside of the carbon as well as inside
- May only form thin layer of alane inside and/or outside
- May only be bulk outside on solvent and amine evaporation under vacuum at 50 °C

Accomplishments and Progress

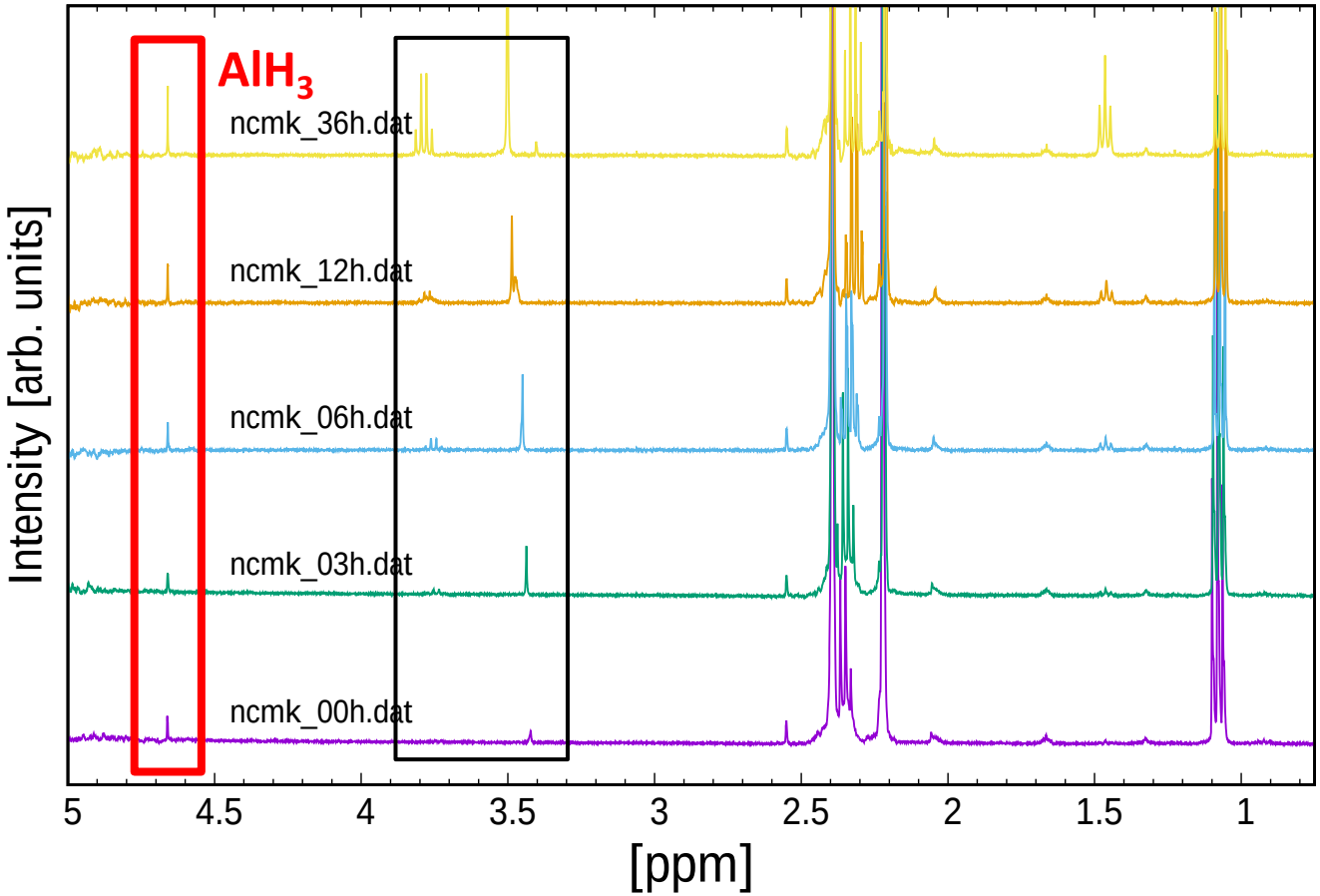
^{1}H Solution NMR Indicates that DMEA is Protonated by Carboxylic Acids Groups in Empty N-doped Carbon (NCMK3-type)



- Pure DMEA (no alane) + NCMK3 carbon
- Amine is being protonated by hydrogen in the carbon structure

Accomplishments and Progress

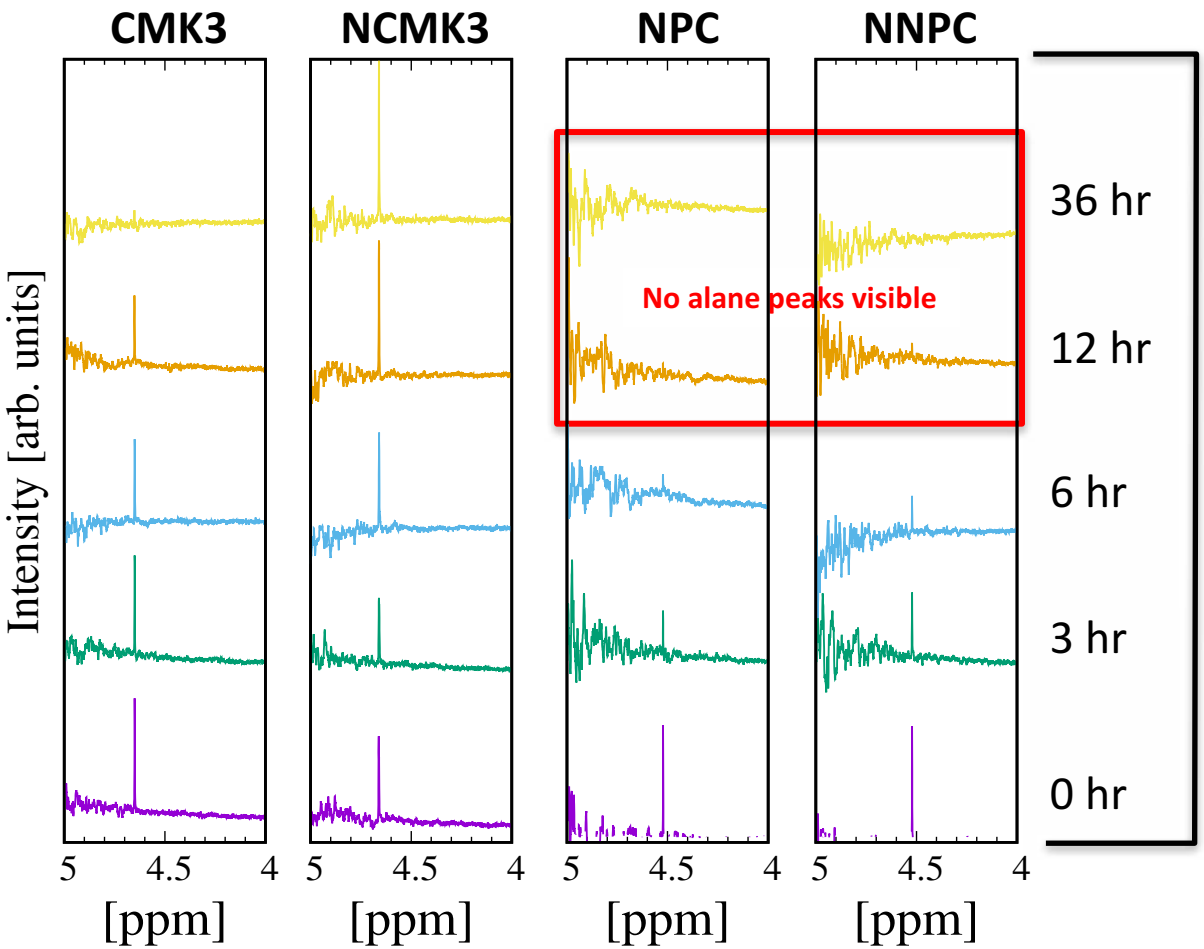
^{1}H Solution NMR of NCMK3 + alane-DMEA Indicates Stronger DMEA Protonation and Alane Remains in Solution



- Stronger amine protonation over time from carboxylic acids
- Persistent AlH_3 signal (narrow peaks indicate it is in solution)
- Alane does not appear to enter the pore structure in CMK3

Accomplishments and Progress

Solution ^1H NMR Suggests Loss of AlH_3 in Solution of NPC-type Carbons



- CMK3: XRD suggests alane may nucleate on the outside of the carbon and block further infiltration

CMK3-type carbons

- NMR indicates alane in solution up to 36 hours
- XRD shows large crystalline material outside the pores

NPC-type carbon

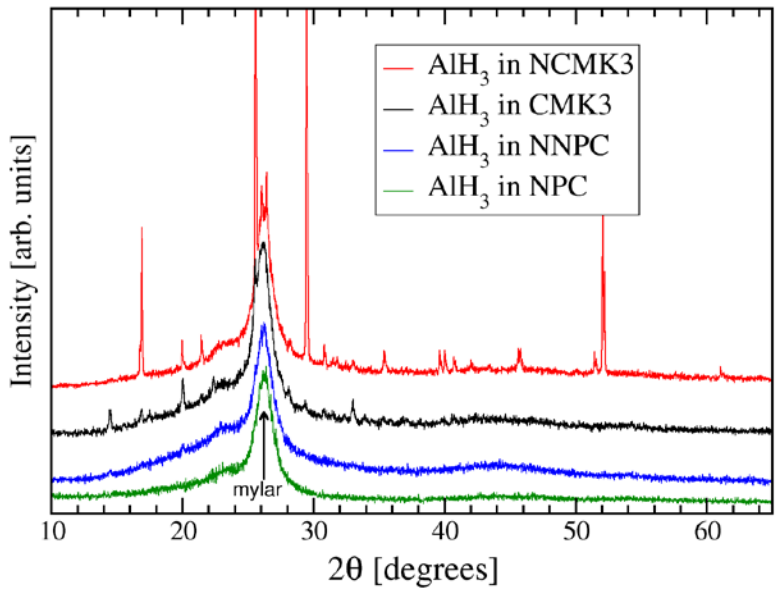
- NMR indicates no alane in solution after 6 hours
- XRD shows no Bragg peaks

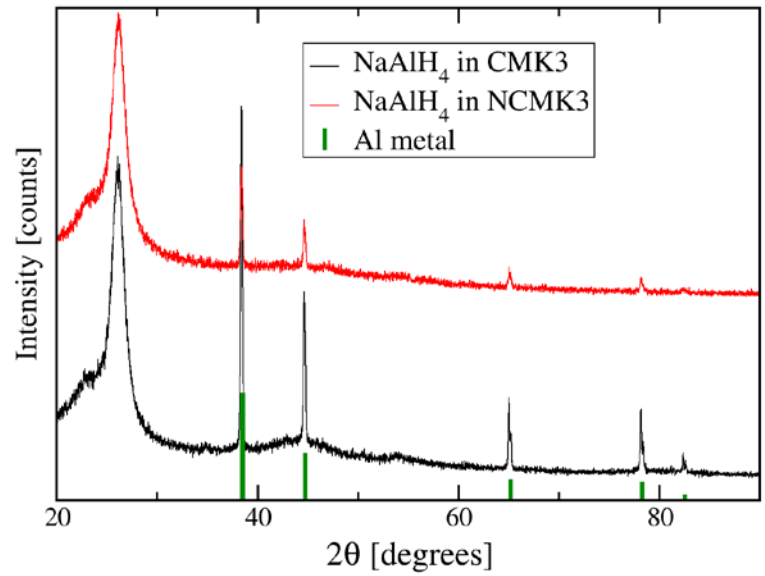
NMR, XRD Data Suggest

- CMK3 may not infiltrate via solution
- NPC may infiltrate via solution

Accomplishments and Progress

XRD Indicates Unknown Phase in AlH_3-infiltrated NCMK3 Carbons and Al metal in $NaAlH_4$-infiltrated Carbons





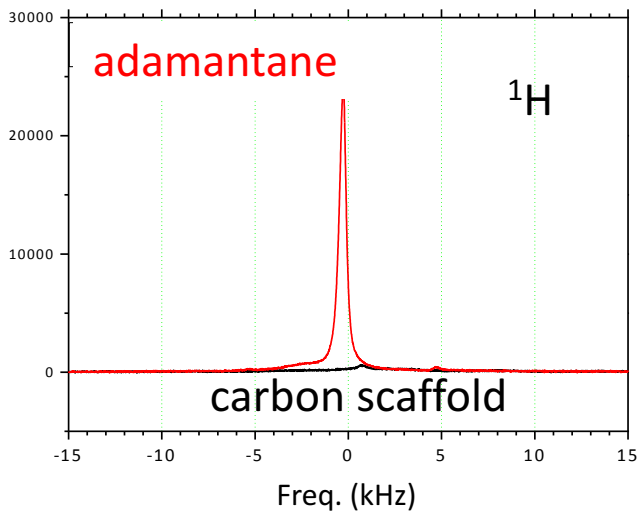
- Unidentified phase in the alane-infiltrated sample, profile fit: 10 f.u. monoclinic structure with cv 330 Å^3
- No ICSD matches: {Al, O, H, Cl, N, C}
- Some overlap with AlH_3 α' phase peaks
- Scherrer length: 70 nm (outside pores)
- NNPC-type carbon shows no peaks and alane may be inside the pores

- Metallic Al indicates some decomposition on infiltration
- Significant hydrogen desorption is still observed
- **No oxide phases present**

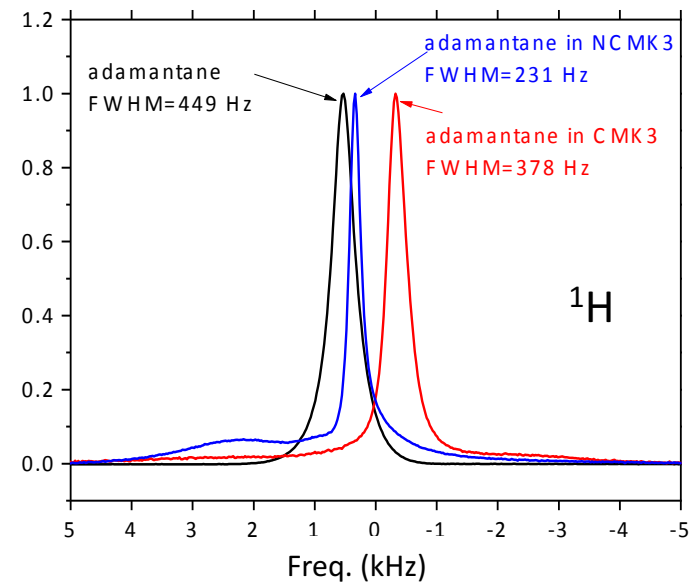
Quantify Solid-state MAS ^{1}H NMR Line Broadening and Shift Due to Carbon Framework

✓ Task 3: Subtask 3.1: Empty carbon characterization via NMR. Y1Q2-Y2Q2

Potential issues for NMR spectra interpretation:
1. Susceptibility of carbon framework
2. Quadrupolar effects



^{1}H background signal from pure carbon scaffold is small

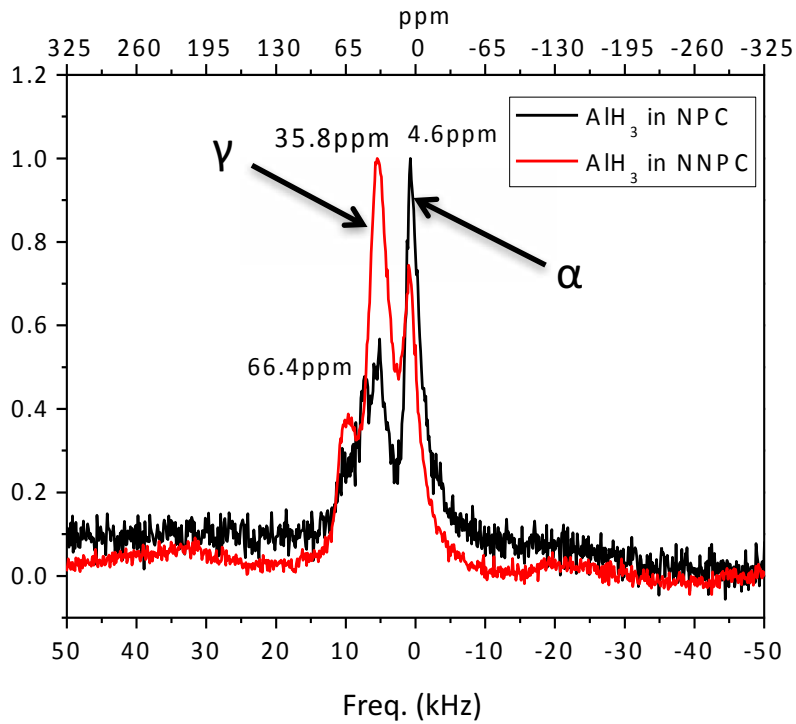


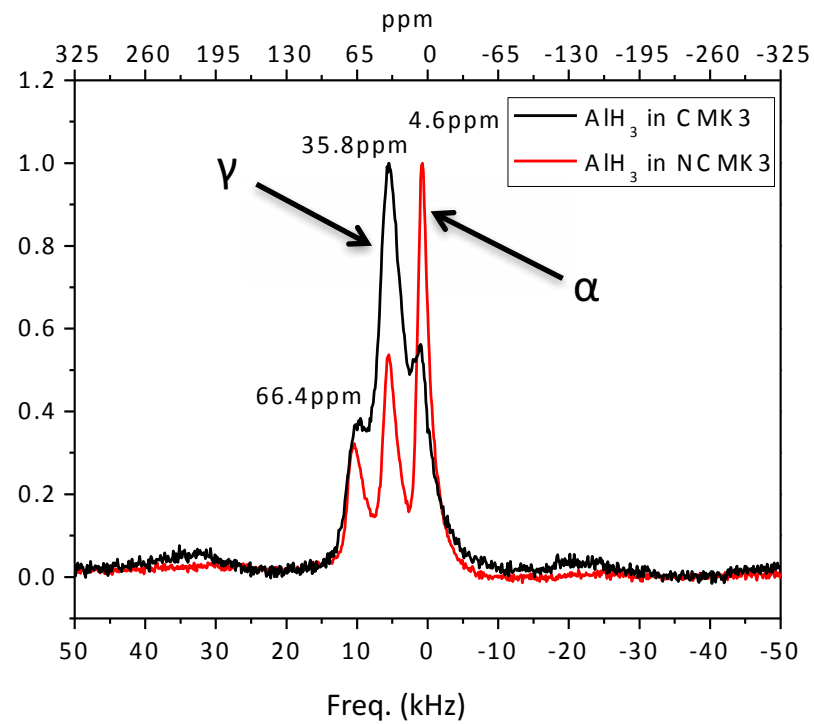
- Adamantane shift <~ 3 ppm, small susceptibility shift
- No significant line broadening for adamantane in carbon

Accomplishments and Progress

^{27}Al MAS NMR of AlH_3-infiltrated CMK3-type Carbons Suggests AlH_3 and Al-oxide May be Present

✓ Task 3: Subtask 3.2: MAS NMR Characterization. Y1Q2-Y2Q2

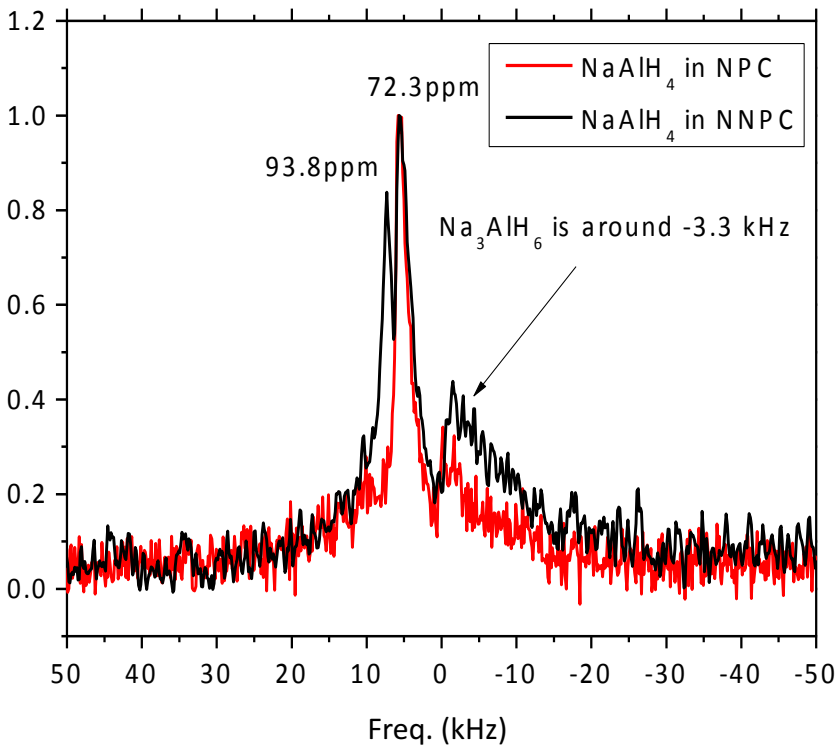


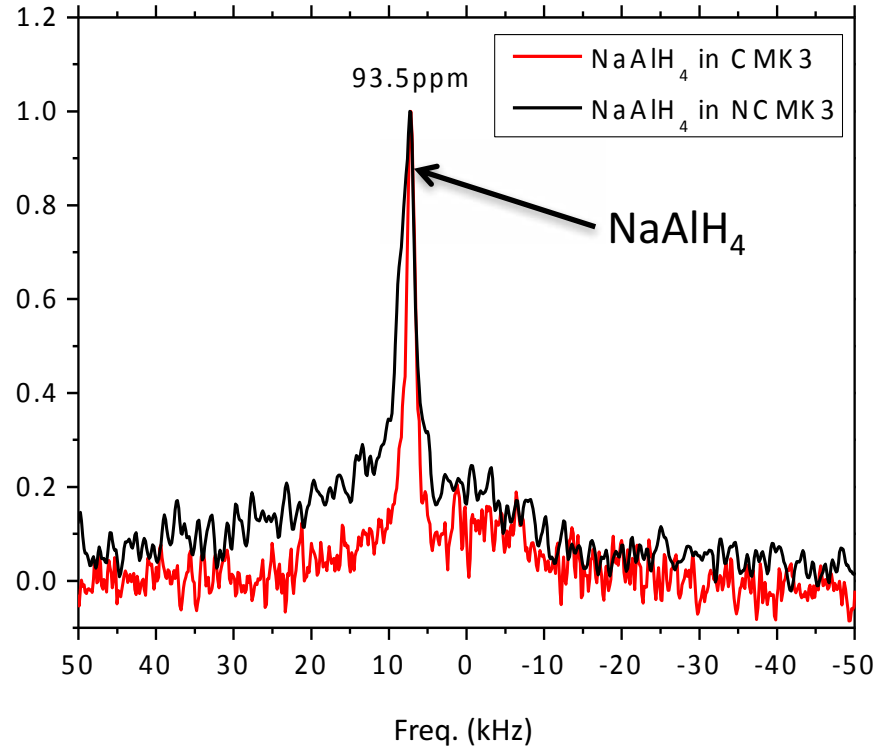


- Alane-like chemical shift and XRD together indicate possible new AlH_3 polymorph
- Aluminum oxide likely during transfer to NMR tubes in a glove bag
- See technical backup slides for table of ^{27}Al chemical shifts

Accomplishment

^{27}Al NMR and XRD Indicate Some Decomposition and $NaAlH_4$ Post-infiltration



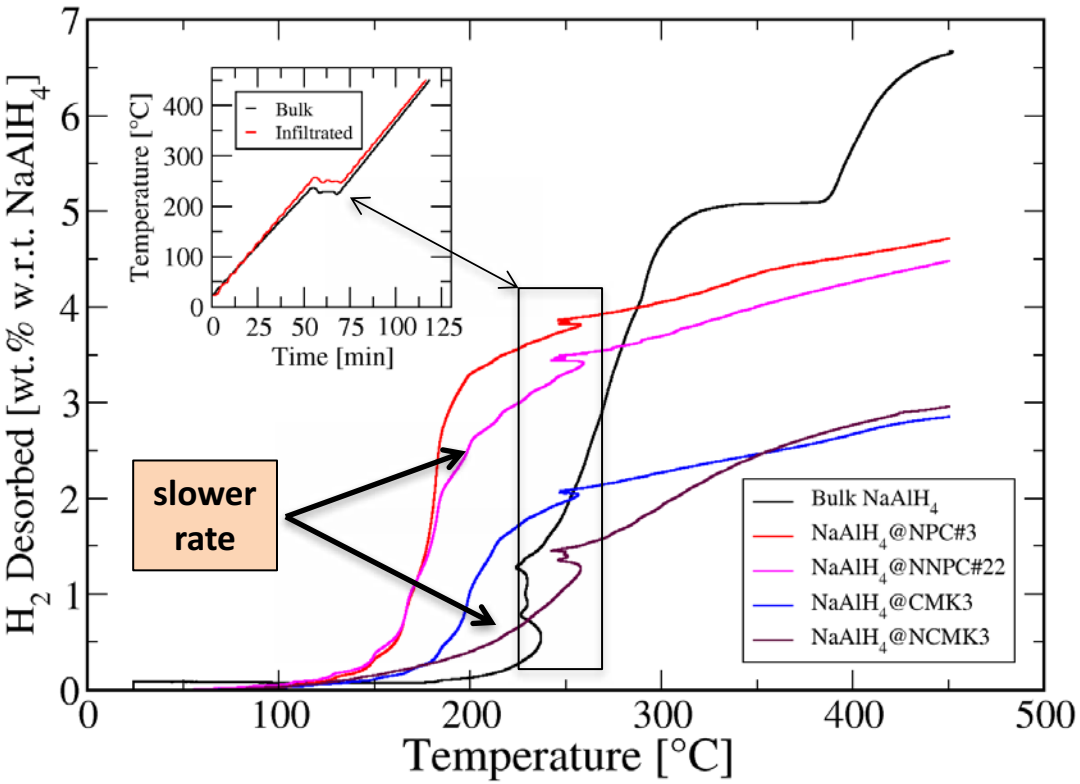


- $NaAlH_4$ ^{27}Al chemical shift is 93.8 ppm
- Possibility of Na intercalation in the hard carbon (see backup slides) -
- No AlH_3 evident in the NMR spectra for $NaAlH_4$-infiltrated samples
- Unknown species at 72.3 ppm in NNPC-type carbon

Accomplishment

Significant Hydrogen Content Remains in Both NPC and CMK3 Carbons After Infiltration with $NaAlH_4$

✓ Task 5: Subtask 5.1: Quantitative gas desorption measurements. Y1Q4-Y2Q2



Summary of Experiments

- No Na intercalation in the hard carbon is evident
- Melt-infiltration with $NaAlH_4$ is possible, but NMR does not indicate presence of alane
- Pore volumes are larger in NPC-type carbons, resulting in larger hydrogen desorption capacity
- Nitrogen doped carbons show slower hydrogen desorption compared to undoped carbons
- Max temperature over 400°C, includes NaH decomposition

Collaborations

- Subcontractors:
  - Washington University (Solid-state MAS NMR)
  - Saint Louis University (Solution infiltration of AlH_3 into carbons)
- HyMARC Partner: Sandia
  - Jim White, Vitalie Stavila, Mark Allendorf (XPS, porosimetry, hydrogen PCT, high pressure hydrogen manifold)
  - Waruni Jayawardana (graduate student at UMSL) performed measurements at SNL/CA
- HySCORE Partner: NIST Center for Neutron Research (NCNR)
  - Christopher Carr (graduate student at UMSL) performed measurements at NIST (with Terry Udovic and Mira Dimitrievska)
- AIST (Japan)
  - Kouji Sakaki and Hyunjeong Kim, high Q synchrotron scattering for pair distribution function (PDF) analysis of local order

Remaining Challenges and Barriers

- Infiltration of AlH_3 in smaller quantities in ^{15}N-doped carbons to demonstrate Lewis acid/base pair for definitive proof of concept (overloading sample may produce alane outside of the pores or make interpretation of the NMR data more difficult)
- Reduce oxygen/water contamination during sample transfer before NMR measurements
- Find alternate routes to introduce Al species inside the carbon pores
- Demonstrate reversibility of alane in functionalized nanoporous carbons

Proposed Future Work

- Infiltration of base-stabilized AlH_3 into ^{15}N-doped carbon samples (SLU)
- Infiltration of $NaAlH_4$ into 15N-doped carbon samples (UMSL)
- Infiltration of $LiAlH_4$ into 15N-doped carbon samples (UMSL/Sandia)
- Continued synthesis of N-doped carbon frameworks to increase N content (UMSL)
- ^{15}N-doped samples to WU for ^{27}Al MAS NMR analysis to determine Lewis acid/base interaction between ^{15}N-^{27}Al
- ^{27}Al solution NMR monitoring over time to determine presence or lack of alane in solution post infiltration (SLU)
- Infiltration at elevated temperature using NPC19/NNPC 19
- Thermal properties of the material through DSC/TGA analysis of pre- and post-infiltrated materials
- High-pressure H_2 absorption experiments at SNL/CA

Accomplishments / Progress Summary

1. Nitrogen-doped carbons have been synthesized and shown by X-ray photospectroscopy to contain pyridinic N (contains lone pairs that may participate in Lewis acid/base chemistry)
2. Two different carbon morphologies have been prepared
   - NPC-type: open, cylindrical pores
   - CMK3-type: smaller, slit-like pores
3. Uptake of AlH_3 from base-stabilized aminated ligands to the framework is suggested by in-situ solution NMR experiments
4. Magic angle spinning nuclear magnetic resonance (MAS-NMR) indicates presence of bulk AlH_3 in solution-infiltrated carbon samples
5. Preparation of ^{15}N-labeled N-doped carbons for advanced NMR techniques (^{15}N is a spin ½ nucleus, no quadrupole moment)
6. Alternate introduction of AlH_3 into N-doped carbons via infiltration of $NaAlH_4$ indicates that sodium alanate may be incorporated into the carbons in contrast to literature using other carbon types
7. A strong interaction between the nanoporous frameworks is evident from both infiltration methods
8. Extensive collaborative effort demonstrated with Sandia/CA through HyMARC and NIST NCNR for neutron scattering studies

Milestone Summary Table For BP1

Task	Milestone/Go/No-Go	Verification	Date
1, Synthesis	Synthesize 15N-doped nanoporous carbon	XPS confirming the presence of pyrN.	Y1Q1 M3
3, NMR	Identify chemical shifts of ^{15}N in carbon	MAS NMR on empty ^{15}N-doped carbons	Y1Q2 M6
2, Infiltration	Infiltration of AlH_3 in ^{15}N-carbons via amine-stabilized AlH_3	NMR	Y1Q3 M9
1, Characterization	Measure activation energies for BH_3- and AlH_3-infiltrated N-doped carbons.	Isothermal dehydriding rate studies	Y1Q4 M12
SMART	Demonstrate increased stability of AlH_3 or BH_3 incorporated into nitrogen-doped carbons	TPD with RGA; DSC; Arrhenius analysis	
SMART	Verify formation of a Lewis-acid/base complex in the N-doped carbons with B-N or Al-N bond signatures verified by NMR chemical shifts	B-N or Al-N bond signatures verified by NMR and hydrogen gas desorption temperatures beginning below 100°C	Y1Q4 M12
1, Synthesis	Vary surface areas and N/C ratios N-doped carbon	Porosimetry	Y2Q1 M15
4, Theory	MG-CLP calculations of stability of the frameworks	DFT	Y2Q2 M18
1&3, NMR and gas desorption Go/No-go	Demonstrate reversible hydrogen absorption and formation of AlH_3 in the pores of nitrogen-doped carbon frameworks at a pressure of less than 180 bar at a temperature at or below 100°C	Sieverts' apparatus	Y2Q2 M18

Acknowledgements

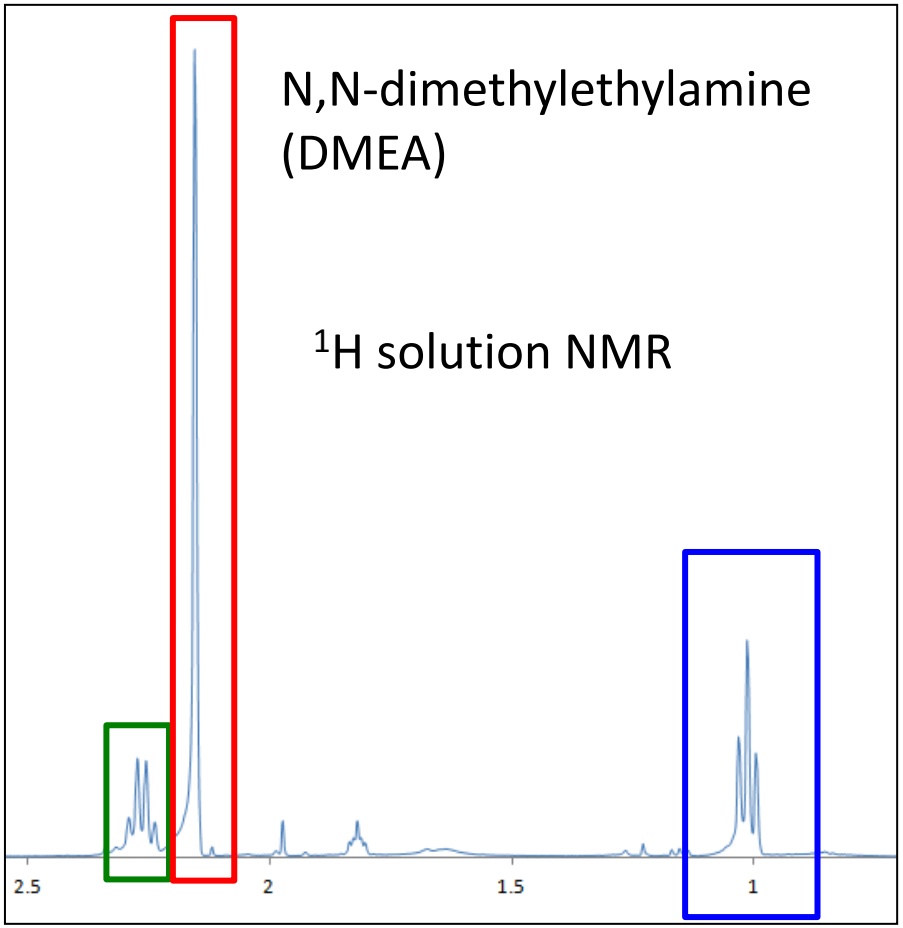
- Department of Energy, Office of Energy Efficiency and Renewable Energy (EERE)
- Ned Stetson
- DOE project officers: Katie Randolph, Zeric Hulvey, Chris Werth
- NSF IGERT program for travel support of neutron scattering work with graduate student Christopher Carr

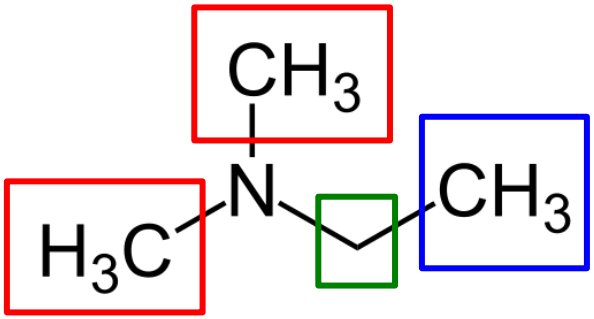
END

Technical Back-Up Slides

Technical Backup Slide

Dimethylethylamine ^{1}H Solution NMR Reference Spectra





- Solvent: deuterated dichloromethane
- Trace water shifts the zero (whole pattern)

Technical Backup Slide

27Al Chemical Shift: Possible Species Include AlH_3, Al-O

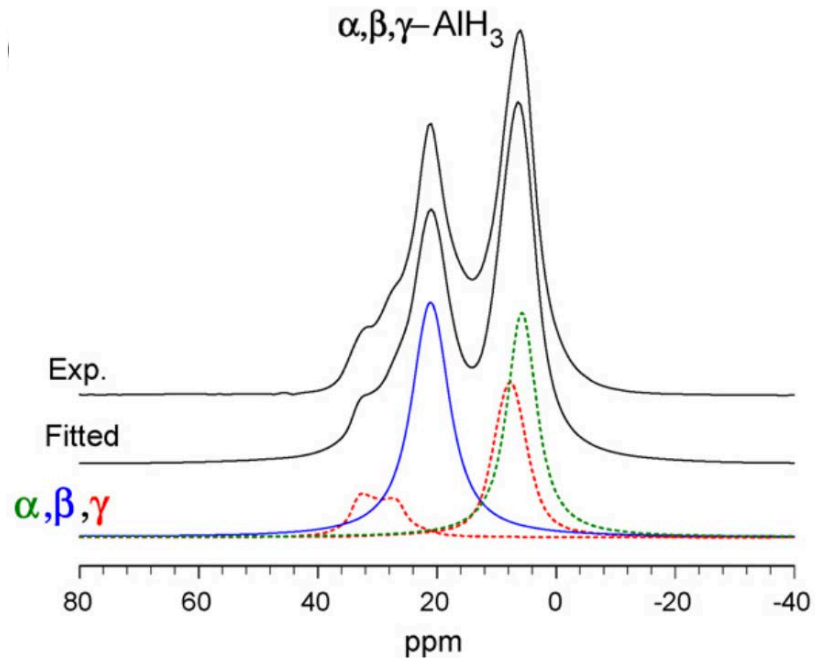
Possible Al-H / Al-O species

^{27}Al:

- $NaAlH_4$ 95.2 ppm
- Na_3AlH_6 -42.7 ppm
- Al metal 1639.5 ppm
- α-AlH_3 5.8 ppm
- β -AlH_3 21.5 ppm
- γ –AlH_3 (1) 10.9 ppm (2) 36.0 ppm
- α -Al_2O_3 16 ppm
- γ-Al_2O_3 (1) 64 ppm (2) 6.0 ppm

^{23}Na:

- $NaAlH_4$ -9.4 ppm
- Na_3AlH_6 (1) 22.8 ppm (2) -10.2 ppm
- NaH 18.3 ppm
- Na metal 1124 ppm

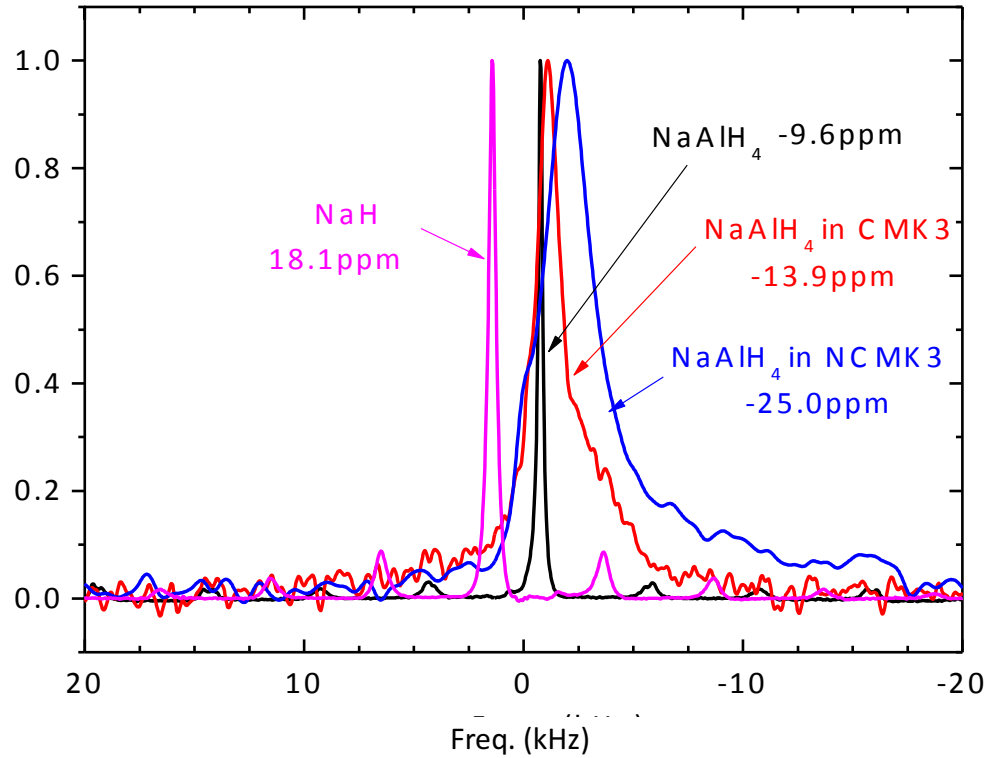


Sample	Code	δ_{iso} (ppm)
α-AlH_3	BNL-H2963	5.8
γ-AlH_3	BNL-H2990	γ-I: 10.9 γ-II: 36.0
α + β + γ-AlH_3	BNL-H2961	21.5[c]

J. Al. Comp., 446, 290, 2007

Technical Backup Slide

Broad ^{23}Na MAS NMR Spectra Indicate Possible Range of Environments

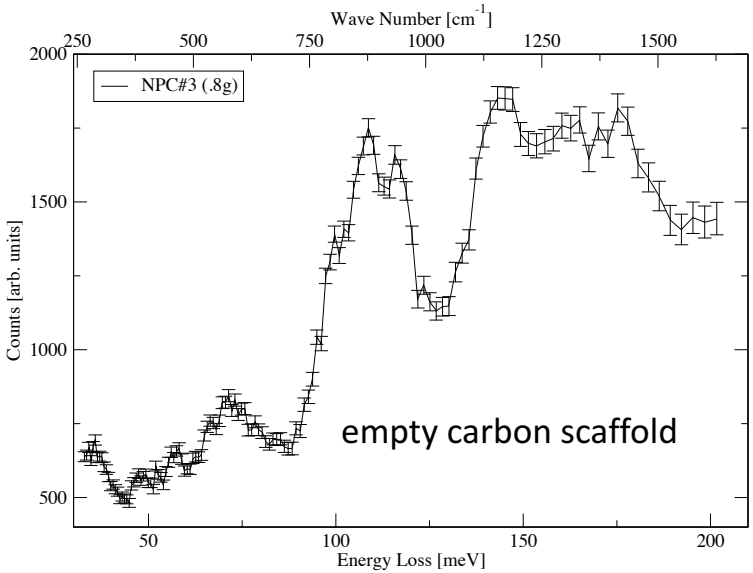


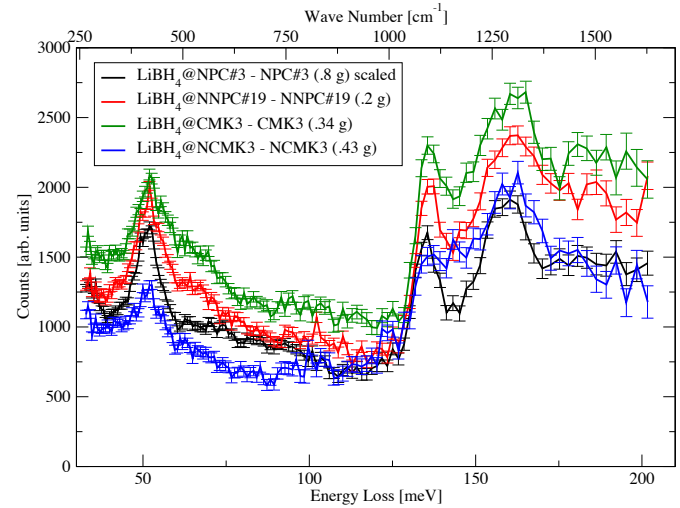
- Shifts may be slightly different due to differing susceptibility in different carbon environments

- K. Gotoh et al., *Journal of Power Sources*, **225** (2013) 137-140
  a) Na intercalates into hard carbon much more easily than in graphite
  b) 5.2 ppm -- reversible sodium stored between disordered graphene sheets
  c) -9 to -16 ppm indicative of Na in closed nanopores
- Na in $NaAlH_4$

Technical Backup Slide

Neutron Vibrational Spectroscopy



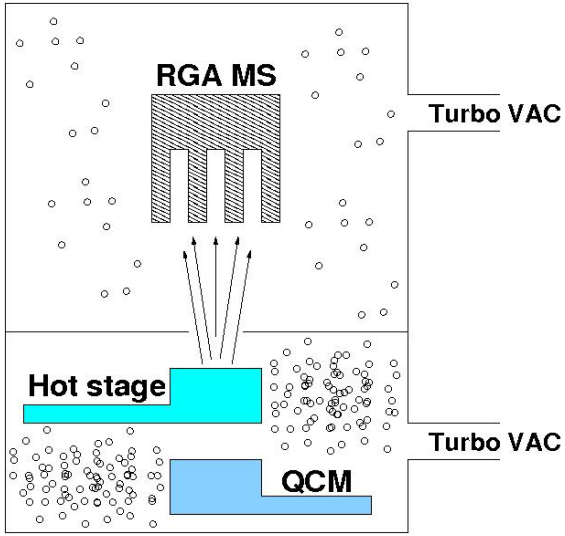


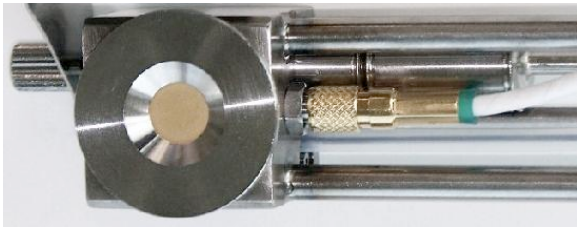
Quasielastic neutron scattering measurements are ongoing in 2017 at the NIST Center for Neutron Research (NCNR) to investigate the dynamics of LiBH4 infiltrated into the nitrogen doped/undoped carbon scaffolds synthesized by our group for this project. This work is collaborative with Terry Udovic at NIST. Through these investigations it should be possible to measure the impact of scaffold nitrogen doping on the dynamics of confined LiBH4, in particular dynamics of substrate pyridinic nitrogen bonded to BH3 molecules produced during partial decomposition on infiltration may be discernable.

This figure represents only contributions from the nanoconfined LiBH4. The peak centered around 52 meV can be assigned to BH4- torsional bands, while the bands at 135 and 160 meV represent BH4- bending modes when compared to the bulk LiBH4 spectra (see ref 4). It is interesting to note the decreased intensity and apparent broadening of 135 meV band for LiBH4@NCMK3 (N-doped carbon) compared to the LiBH4@CMK3 (undoped) sample, which may signify an interaction between the substrate nitrogen and BH4- or BH3 species. Upcoming QENS measurements will allow further investigation into this possibility. To quantify the amount of hydrogen and nitrogen (doped samples) present in the carbon scaffolds prompt gamma activation analysis (PGAA) measurements will be performed at NCNR.

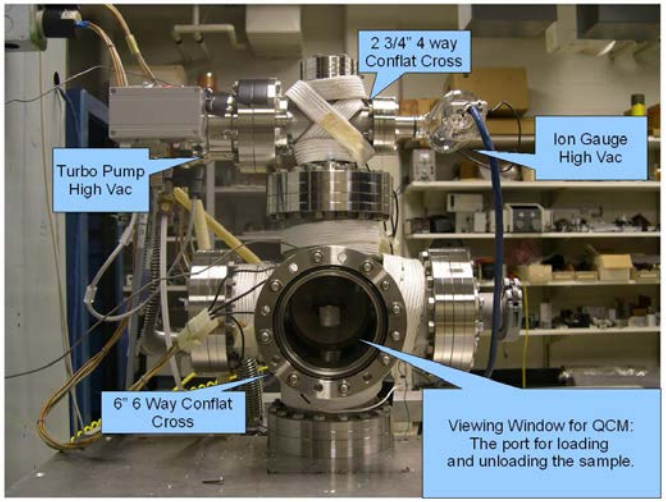
Technical Backup Slide

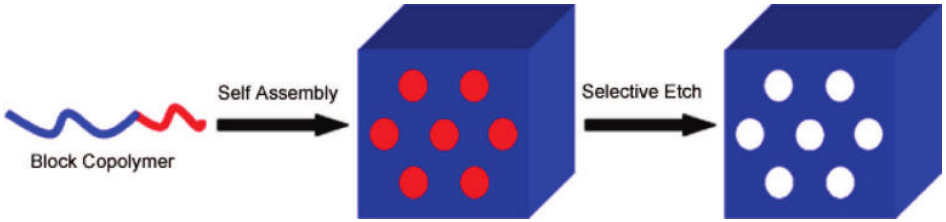
Direct Line-of-sight Hot Stage For Desorbed Gas Studies Will Follow Reaction Pathways



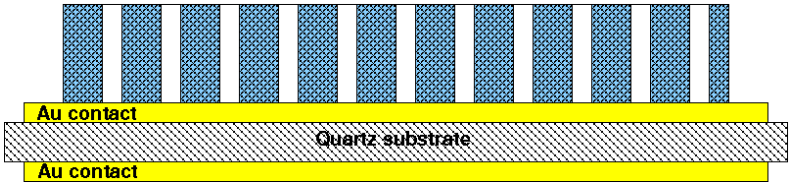


QCM / crystal
Tangidyne, Inc.



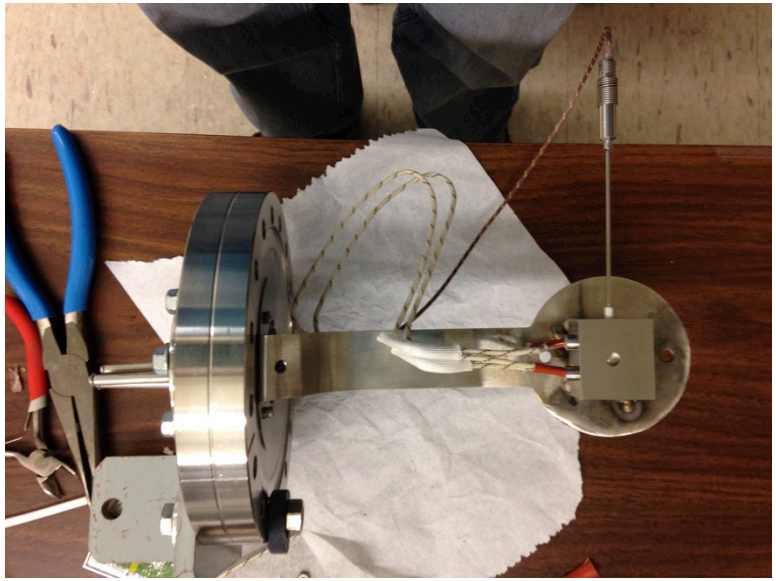


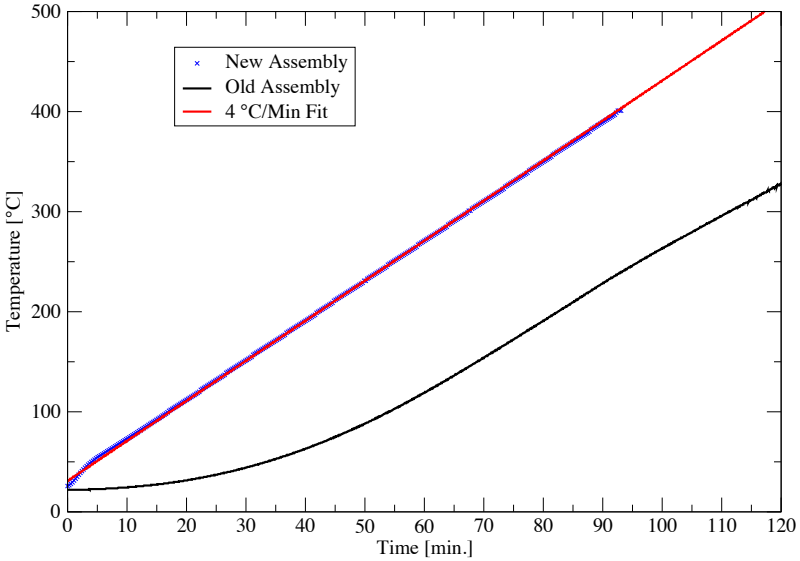
Aligned columns



Technical Backup Slide

Direct Line-of-Sight Hot Stage Rebuilt for Better Temperature Control TPD





Publications and Presentations

- "*The Chemistry and Physics of Energy Storage Materials at the Nanoscale*", E.H. Majzoub, Science in St. Louis, Nov 2016
- "*Surface Functionalized Nanoporous Carbons for Kinetically Stabilized Complex Hydrides through Lewis acid-Lewis base Chemistry* ", Chris Carr, TMS annual meeting, Feb 2017
- "*Surface Functionalized Nanoporous Carbons for Kinetically Stabilized Complex Hydrides through Lewis acid-Lewis base Chemistry* ", C. Carr, W. Jayawardana, E.H. Majzoub, St. Louis Regional Materials Network Meeting , Oct 2016
- "*Influence of Functionalized Nanoporous Carbons on the Properties of Confined* $NaAlH_4$," C. Carr, W. Jayawardana, E.H. Majzoub, Missouri Inorganic Day, 06 May, 2017