

IV.C.10 HyMARC Seedling: Fundamental Studies of Surface-Functionalized Mesoporous Carbons for Thermodynamic Stabilization and Reversibility of Metal Hydrides

E.H. Majzoub

University of Missouri–St. Louis
One University Blvd
St. Louis, MO 63121
Phone: (314) 516-5779
Email: majzoub@umsl.edu

DOE Manager: Katie Randolph
Phone: (240) 562-1759
Email: Katie.Randolph@ee.doe.gov

Subcontractors:

- Saint Louis University, St. Louis, MO
- Washington University, St. Louis, MO

Project Start Date: October 1, 2017
Project End Date: March 30, 2018

Overall Objectives

- Reach the DOE hydrogen storage targets of 70 g/L H₂ using a reversible metal hydride.
- Render alane (AlH₃) reversible at temperatures around 100°C and pressures accessible at compressed gas filling stations.

Fiscal Year (FY) 2017 Objectives

- Prepare nitrogen-doped nanoporous carbon frameworks and quantify the N/C ratio and the amount of nitrogen that is pyridinic (able to form Lewis-acid/base complexes).
- Incorporate alane into N-doped carbon frameworks in solution using base exchange with dimethylethylamine-alane (DMEAA).
- Incorporate alane into N-doped carbon frameworks via melt-infiltration using alanates with cations that may intercalate into the carbon (e.g., Li, Na) leaving alane to complex with pyridinic nitrogens in the framework.
- Demonstrate Lewis-acid/base complex of alane via solid-state nuclear magnetic resonance (NMR) on 15N-doped carbon frameworks infiltrated with alane via solution base-exchange.

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan.

- (A) System Weight and Volume
- (E) Charging/Discharging Rates

Technical Targets

Surface-Functionalized Nanoporous Carbons for Complex Hydride Confinement and Reversibility

This project is conducting fundamental studies of nitrogen-doped, ordered nanoporous carbons with specific surface functionality. Pyridinic nitrogen atoms contained in the carbon structure have “lone pair” electrons capable of acting as a Lewis base and coordinating with alane (AlH₃), forming a Lewis-acid/base complex. Information about the interactions between alane and these pyridinic nitrogens in a nanoframework environment will be used to tune the synthesis and structure of these frameworks to optimize their storage characteristics and meet the following DOE 2020 hydrogen storage system targets.

- System Gravimetric Capacity: 4.5 wt%
- System Volumetric Capacity: 30 g H₂/L

FY 2017 Accomplishments

- Preparation of nitrogen-doped nanoporous (10–20% N) frameworks with pyridinic nitrogen.
- Characterization of N-doped carbons with N₂ adsorption porosimetry, X-ray photoelectron spectroscopy (XPS), NMR, and X-ray diffraction (XRD).
- Infiltration of alane via base-exchange from DMEAA.
- Infiltration of alanate via the melt from sodium alanate.
- In situ ¹H solution NMR of alane-infiltration experiments with DMEAA and carbon frameworks in dichloromethane solution.
- Characterization of alane-infiltrated carbons using XRD, and magic angle spinning (MAS) NMR for the nuclei ¹H, ²⁷Al, and ²³Na.



INTRODUCTION

Metal hydrides used for applications today have a low hydrogen weight percent, e.g., 1.1 wt% H₂ for LaNi₅H₆, due to the much heavier transition metal elements. The light metal hydrides, including sodium alanate (NaAlH₄), have a much larger weight percentage of hydrogen but suffer from poor kinetics and reversibility because of phase separation of the components—aluminum metal in the case of sodium alanate. Although many light metal hydrides such as pure alane (AlH₃) and many complex light metal hydrides are known, most are either too stable, requiring high temperatures to drive the hydrogen off, or too unstable and difficult to rehydride under safe hydrogen pressures at reasonable temperatures. In order to reach the DOE volumetric and gravimetric targets the light metals must be utilized and these problems must be overcome. The goal of this project is to render light metal hydrides like AlH₃ reversible under moderate conditions.

APPROACH

Our approach is to perform fundamental studies on functionalized porous carbons (FPC) doped with nitrogen heteroatoms to understand the mechanisms of thermodynamically stabilized high-capacity metal hydrides (MH). Ultimately, our goal will be to stabilize alane (AlH₃) in a nanoporous carbon framework through Lewis-acid/base interactions provided by pyridinic nitrogen on the interior wall of the carbon framework. This capping layer should provide the kinetic stabilization analogous to that of the oxide layer on bulk alane that allows it to be stable in air for many years despite the relative instability of the compound. More importantly, in very small pores this interaction is expected to solvate and increase the enthalpy change of alane dehydriding. This approach is plausible for two reasons. (1) Ligand-stabilized alane chemistry is well known and understood (e.g., triethylenediamine-stabilized alane, and other amine-stabilized alanes) and the pyridinic nitrogen in the pore walls of the carbon may effectively solvate the surface of alane infiltrated in the pores of the framework. (2) The quantity of pyridinic and pyrrolic nitrogen is quantifiable in hard carbon templates using XPS. The proposed concept capitalizes on recently discovered nanoporous hosts capable of binding metal hydride particles and altering the kinetics and thermodynamics of H₂ release and absorption. Computational guidance of synthetic activities by a suite of validated modeling tools will be used to efficiently converge on the best hydride and doped carbon materials. This approach allows for a systematic variation in the MH-FPC interactions, enabling the thermodynamics to be tuned to achieve materials with greater than 70 g H₂/L. Our preliminary experimental results show that nanostructured MH materials are stabilized in N-doped carbons, with activation energies of desorption increased over 30 kJ/mol compared to undoped carbons. This will pave

the way for practical applications of binary and complex metal hydrides that are not practically reversible in bulk, but can be fully cycled under mild conditions when confined inside nanoporous frameworks displaying strong surface interactions with MH nanoparticles.

RESULTS

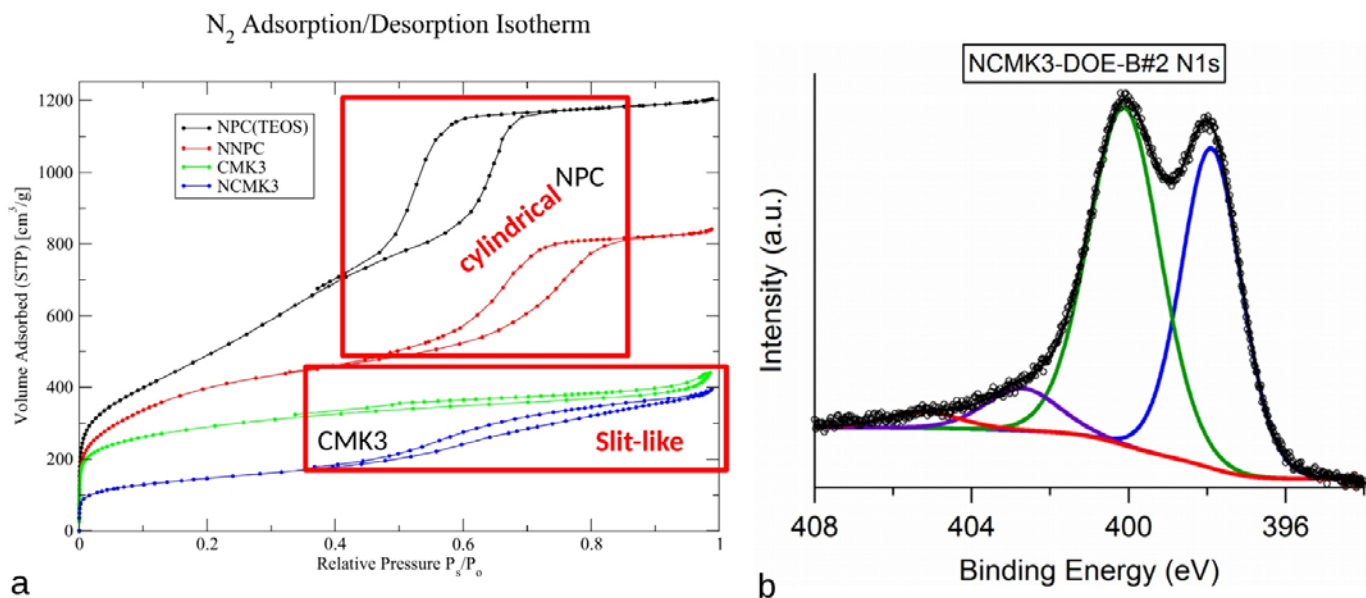
Preparation of nitrogen-doped nanoporous carbons: Two types of nanoporous carbons (NPC) have been prepared for investigation. (1) NPC-type carbons have open cylindrical pores resulting in steep N₂ adsorption profiles. These carbons are prepared from phenolic resins that are the carbon precursor, and block co-polymer templates that give the resulting pore morphology [1]. (2) CMK3-type carbons are prepared from a carbon precursor such as sucrose (no ring structure in the precursor) and use SBA-15 nanoporous silica as the template that is etched out with HF after calcination [2]. Figure 1a shows nitrogen adsorption data for these carbons. Prepared carbon frameworks that contain nitrogen precursors are designated with an “N” before the type or morphology of the carbon, i.e., CMK3-type carbons containing nitrogen are designated NCMK3.

It is important in the N-doped carbons that the electronic structure of the nitrogen contains a lone pair of electrons like that in the molecule pyridine. This nitrogen is called pyridinic and may be quantified with XPS. XPS results are shown in Figure 1b and indicate the presence of pyridinic nitrogen (about 1/3 of the all of the nitrogen in the sample).

Infiltration of NNPC and NCMK3 with alane via base exchange: In order to incorporate alane into the N-doped carbons, we attempted a base exchange using dimethylethylamine (DMEA). The basic concept is that pyridinic nitrogen in the pore wall will provide stronger binding to alane than will the DMEA, and the alane will switch bases. A solution of DMEAA in dichloromethane was introduced to N-doped carbons as shown in Figure 2a.

If alane exchange to the framework occurs during exposure of the carbons to the DMEAA in solution, there will be free DMEA in solution that may be quantified with solution ¹H NMR. In our results, shown in Figure 2b, the shift observed in the NMR spectra for DMEA indicated not only that the alane exchanged with the framework, but that the newly free DMEA was becoming protonated. The shifts in the ¹H spectra were confirmed by comparing the DMEAA-exposed carbons with a control sample of DMEA protonated with HBF₄.

Figure 3 shows the ¹H proton peak from alane for both non-N-doped carbons (NPC, CMK3) and N-doped carbons (NNPC, NCMK3). It is clear from the NPC and NNPC panels that the alane peak diminishes in intensity and disappears around 6 h, while in the CMK3-type carbons the alane peak persists and may even become narrowed. The narrow nature of the peaks in solution NMR is due to



STP – Standard temperature and pressure

FIGURE 1. (a) Nitrogen adsorption porosimetry of bare and N-doped carbons showing both slit like and cylindrical pore structures. (b) N 1s spectra of the NCMK3-type carbon. Four different bonding environments pyridinic (blue), pyrrolic (green), graphitic (violet) and oxidized (red) are shown in the figures. Data taken at Sandia National Laboratories, California, by Jim White.

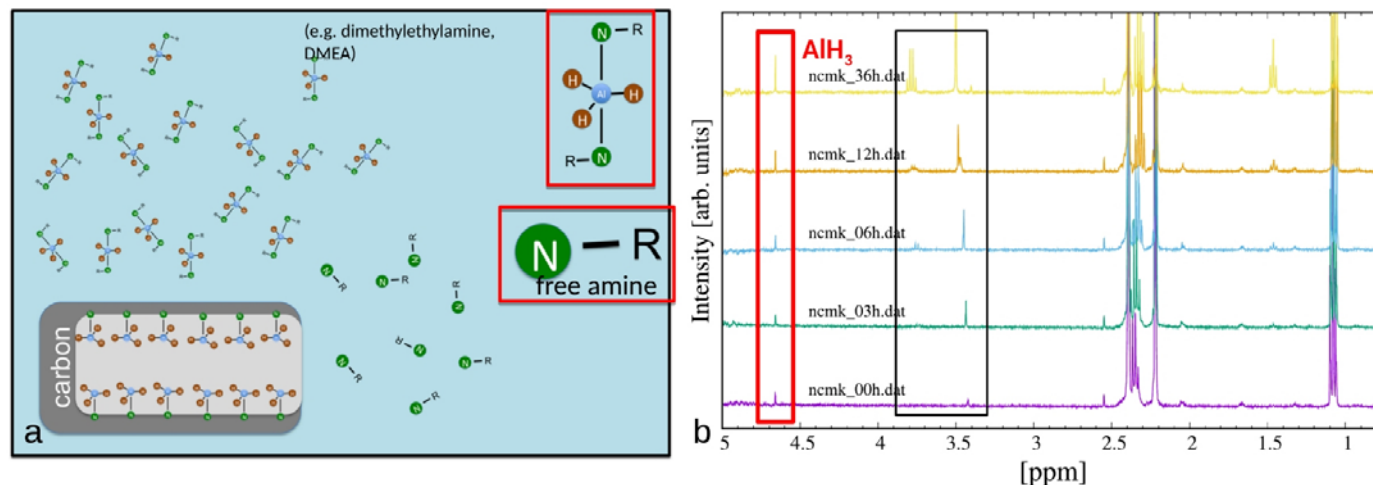


FIGURE 2. (a) Cartoon showing the exchange of alane from DMEA to the carbon, leaving free DMEA in solution. (b) In situ ¹H solution NMR spectra of NCMK3-type carbon exposed to DMEA in solution.

rapid molecular tumbling. Their absence suggests that in the NPC-type carbons the alane is no longer in solution; it has either decomposed and is gone, or has attached to some larger structure such that the ¹H peak is no longer visible. In contrast, the CMK3-type carbons show a persistent alane peak that does not diminish, except for late times in the CMK3 spectra, suggesting that the alane remains in solution and may not exchange with the CMK3 framework.

It is important to determine whether infiltration attempts result in material internal or external to the nanopores. In wide-angle XRD one looks for Bragg peaks with a width

corresponding to a coherence length larger or smaller than the pore size determined from N₂ porosimetry measurements. XRD spectra following solvent evaporation of alane-exposed samples at a ratio of AlH₃:N of 4:1 are shown in Figure 4a. The narrow peaks from the trace in green indicate that the NCMK3 sample contains material outside the pores. These peaks do not match any known phases containing any combination of {Al,O,N,C,H}. They do, however, have some correspondence with a reported phase of alane (α') [3,4], and may indicate a new polymorph of alane. One possibility may be that the surface interaction of the alane coming

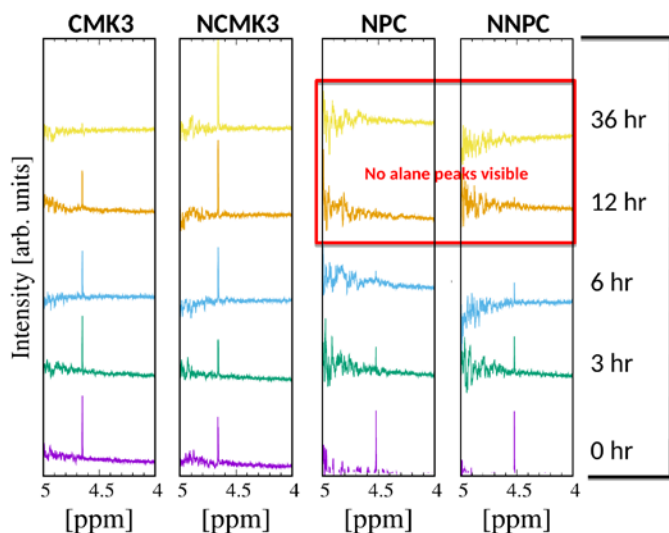


FIGURE 3. In situ ^1H solution NMR spectra of bare and N-doped carbons exposed to DMEAA in solution. NPC-type carbons indicate likely uptake of alane.

out of solution nucleates a metastable phase of alane that is visible in the XRD. Neither NPC nor NNPC samples show any Bragg peaks, indicating any alane in the sample is either amorphous or inside the pores if it did not decompose.

Figure 4b shows ^{27}Al MAS NMR spectra of the samples in panel (a). The triplet of peaks in the NCMK3 spectra is indicative of Al-oxide species [5], but no Al-oxide was found in the XRD spectra, suggesting some oxidation took place during sample transfer before NMR measurements. The spectra from the CMK3, NPC, and NNPC samples are not conclusive, but suggests possible α -alane at 4.6 ppm, γ -alane at 35.8 ppm and an unknown phase at 66.4 ppm.

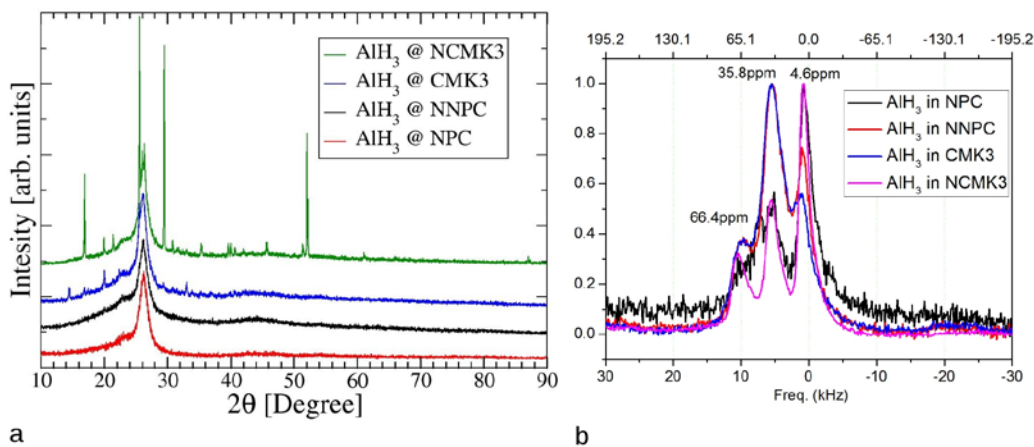


FIGURE 4. (a) XRD spectra of alane-infiltrated carbons showing external material in the CMK3-type carbons indicating a possible new polymorph of alane, but external to the pores, while the NPC-type carbons show no Bragg peaks, suggesting uptake of the alane. The wide peak at 26 degrees is from a mylar film used to minimize air exposure to the samples during measurement. (b) MAS ^{27}Al NMR of the carbons in panel (a) with peak positions showing possible alane with some oxidized Al in the samples.

Preliminary computational results not shown here indicate that base-exchange of AlH_3 should occur from DMEAA to the N-doped carbon substrates, as well as some hydrogen-terminated non-N-doped carbon substrates.

Work not included in this report is the infiltration of the nanoporous carbons using alanates whose cation may intercalate into the carbon itself, delivering a large amount of alane to the pores. These experiments include both NaAlH_4 and LiAlH_4 . Melt-infiltration with sodium alanate indicates that a large amount of alanate is incorporated into the carbons, and is reversible. While MAS ^{27}Al NMR measurements indicate alanate in the pores, there is no indication of alane in the pores. MAS ^{23}Na NMR is inconclusive on the presence of any intercalated Na due to the width of the resonance. Additional experiments using lithium alanate will be attempted due to the clear preference of Li over Na to intercalate into carbon.

CONCLUSIONS AND UPCOMING ACTIVITIES

The project has demonstrated that nitrogen-doped porous carbons with differing types of pore structure interact very differently with base-stabilized alane depending on the synthesis method and resulting pore structure of the carbon. Our preliminary results indicate that CMK3-type carbons may not infiltrate via base-exchange with DMEAA, while NPC-type carbons appear to do so. We have prepared isotopically-labeled ^{15}N -doped carbons for the critical MAS NMR measurements that will investigate the nature of the Al-N interaction and determine whether the Lewis-acid/base complex is forming. In addition to these experiments, we are beginning to investigate the hydrogen release from the N-doped carbons infiltrated with alane using our residual

gas mass spectrometer system at University of Missouri–St. Louis. The sensitivity of this instrument will allow us to examine the reversibility of small samples if those samples are desorbed and rehydrated.

FY 2017 PUBLICATIONS/PRESENTATIONS

1. “LiBH₄ in Aerogel: Ionic Motions by NMR,” Hongyang Zou, Anton Gradišek, Samuel B. Emery, John J. Vajo, and Mark S. Conradi, Hydrogen-Metal Systems (GRS), Gordon Research Seminar, July 15–16, 2017.
2. “Surface Functionalized Nanoporous Carbons for Kinetically Stabilized Complex Hydrides through Lewis acid-Lewis base Chemistry,” Christopher L. Carr, Eric H. Majzoub, TMS 2017 Annual Meeting and Exhibition, February 2017.
3. “Influence of Functionalized Nanoporous Carbons on the Properties of Confined NaAlH₄,” Christopher L. Carr, Waruni Jayawardana, University of Missouri St. Louis Graduate Research Fair, April 2017.
4. “Surface-functionalized Mesoporous Carbons for Electrochemical and Hydrogen Storage Applications,” Gordon Research Conference on Metal-Hydrogen Systems, Stonehill College, MA, July 16–21, 2017.
5. “The Chemistry and Physics of Energy Storage Materials at the Nanoscale,” E.H. Majzoub, Science in St. Louis Series, Academy of Science of St. Louis, St. Louis, MO, November 15, 2016.
6. “Influence of Functionalized Nanoporous Carbons on the Properties of Confined NaAlH₄,” Christopher Carr, Waruni Jayawardana, Eric Majzoub, Missouri Inorganic Day, May 15, 2017.
7. “Influence of Functionalized Nanoporous Carbons on the Properties of Confined NaAlH₄,” Christopher Carr, Waruni Jayawardana, Eric Majzoub, Graduate Research Fair- University of Missouri St Louis, April 28, 2017.

REFERENCES

1. Meng, Y.; Gu, D.; Zhang, F.; Shi, Y.; Cheng, L.; Feng, D.; Wu, Z.; Chen, Z.; Wan, Y.; Stein, A.; Zhao, D. *Chem. Mater.*, 18, 4447, (2006).
2. Carr, C.L., Majzoub, E.H., *J. Phys. Chem. C*, 120, 11426–11432, (2016).
3. M. Paskevicius, D.A. Sheppard, C.E. Buckley, *J. Alloy. Comp.*, 487, 370–376, (2009).
4. H.W. Brinks, A. Istad-Lem, B.C. Hauback, *J. Phys. Chem. B*, 110, 25833–25837, (2006).
5. E.H. Majzoub, J.L. Herberg, R. Stumpf, S. Spangler, R.S. Maxwell, *J. Al. Comp.*, 394, 265-270, (2005).