IV.B.8 Chemical Hydride Rate Modeling, Validation, and System Demonstration

Troy A. Semelsberger (Primary Contact),
Dusan Spernjak, and Jose I. Tafoya
Los Alamos National Laboratory
MS J579, P.O. Box 1663
Los Alamos, NM 87545
Phone: (505) 665-4766
Email: troy@lanl.gov

DOE Managers
Ned Stetson
Phone: (202) 586-9995
Email: Ned.Stetson@ee.doe.gov
Jesse Adams
Phone: (720) 356-1421
Email: Jesse.Adams@ee.doe.gov

Project Start Date: February 2009
Project End Date: June 2015

Overall Objectives

- Develop an automotive chemical hydrogen storage system capable of meeting all of the 2020 DOE targets simultaneously
- Develop and validate chemical hydrogen storage system models
- Quantify viable chemical hydrogen storage material properties that will meet DOE 2020 technical targets with our current system
- Develop and demonstrate "advanced" (non-prototypical) engineering concepts

Fiscal Year (FY) 2015 Objectives

- Design, build, and demonstrate high-pressure, low-temperature thermal conductivity cell to measure thermal conductivities of MOF-5 (metal organic framework) compacts
- Quantify MOF-5 thermal conductivities as a function of hydrogen pressure (<100 bar) and temperature (-196°C)

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
(B) System Cost
(C) Efficiency
(D) Durability/Operability
(E) Charging/Discharging Rate
(F) Codes and Standards
(G) Materials of Construction
(H) Balance of Plant (BOP) Components
(J) Thermal Management
(K) System Life-Cycle Assessment
(R) By-Product/Spent Material Removal

Technical Targets

Our objectives in the last year of the Hydrogen Storage Engineering Center of Excellence were to design, build, and demonstrate a high-pressure, low-temperature thermal conductivity cell to measure the apparent thermal conductivity of engineered MOF-5 compacts under elevated hydrogen pressures (<100 bar) and low temperatures (-196°C to 18°C). There are no technical targets to which our work can be related; however, our work directly supports system modeling and validation of modular adsorption tank insert adsorbent systems.

Accomplishments

- Designed, built, and demonstrated the first thermal conductivity cell for measuring MOF-5 thermal conductivities at elevated hydrogen pressures (<100 bar) and liquid nitrogen temperatures
- Quantified MOF-5 isotropic and anisotropic thermal conductivities at elevated hydrogen pressures

✧ ✧ ✧ ✧ ✧

INTRODUCTION

Hydrogen storage systems based on adsorbents require accurate and reliable measurements of the overall or apparent thermal conductivities operating under realistic operating conditions (i.e., liquid nitrogen temperatures and hydrogen pressures of 100 bar) in order to design and implement the most efficient thermal management system while also minimizing the mass, volume, and cost. In addition, the overall thermal conductivities must be measured in order to validate the system-level adsorbent models.

RESULTS

Isotropic Thermal Conductivity Measurements of Engineered MOF-5 Compacts

Shown in Figure 1 are the measured isotropic or bulk thermal conductivities of neat MOF-5 engineered compacts as a function of pressure (absolute) with helium and hydrogen. All measurements were performed at 16°C. The diameter and height of the engineered MOF-5 compacts were 5 cm and 1.5 cm, respectively. The density of MOF-5 compact was 0.4 g/mL. Ford Motor Company prepared the MOF-5 engineered compacts, and BASF provided the MOF-5 material. The sample did not contain any thermal conductivity enhancement additives (e.g., expanded natural graphite, ENG). The isotropic or bulk thermal conductivity of neat MOF-5 under vacuum (20 in Hg) was measured to be 0.133 W/m K. In both cases (hydrogen and helium), the apparent thermal conductivity increased with increasing pressure. The largest increase in the apparent thermal conductivity was observed for pressures up to around 30 bar. For pressures greater than 30 bar, the apparent thermal conductivity asymptoted to limiting values of 0.3 W/m K with helium and 0.33 W/m K with hydrogen. The differing apparent thermal conductivities of MOF-5 observed with hydrogen and helium can be attributed to the differing gas-phase thermal conductivities of hydrogen (0.1655 W/m K) and helium (0.1411 W/m K). The gas phase contribution to the increase in the apparent thermal conductivity is significant, with nearly a two-fold increase observed as compared to the thermal conductivity of evacuated neat MOF-5.

Anisotropic Thermal Conductivity Measurements of Engineered MOF-5 Compacts

Shown in Figure 2 are the measured anisotropic thermal conductivities of neat MOF-5 engineered compacts as a function of pressure (absolute) with helium at 16°C. All measurements were performed at 16°C. The samples are the same as those used for the isotropic measurements. The anisotropic measurements quantify the axial and radial contributions of the thermal conductivity. Analogous to the isotropic measurements, the axial and radial thermal conductivities are asymptotic with pressure. For pressures greater than 30 bar, the axial and radial thermal conductivities are insensitive to changes in pressure. The limiting values for the radial and axial thermal conductivities are 0.27 W/m K and 0.33 W/m K, respectively. The numbers above the data points in Figure 2 denote the order in which the measurements were made and indicate that there does not appear to be hysteresis. The dashed line in Figure 2 is the weighted contributions of the radial and axial thermal

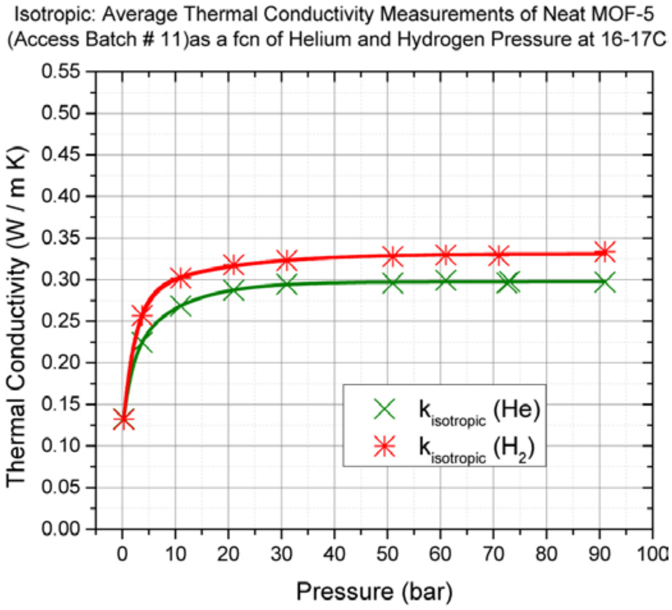

FIGURE 1. Isotropic (bulk) thermal conductivities of neat MOF-5 engineered compacts (diameter = 5 cm, height = 1.5 cm, ρ = 0.4 g/mL) as a function of pressure (absolute) and gas type at 16°C *(all samples were treated in an ultra-high-purity [UHP] N_2 purged oven at 160°C for a minimum of two days, followed by vacuum treatment for 12 hours; average standard deviations for isotropic and anisotropic measurements were ±0.0052 W/m K [helium, 137 measurements] and ±0.0033 W/m K [hydrogen, 104 measurements])*

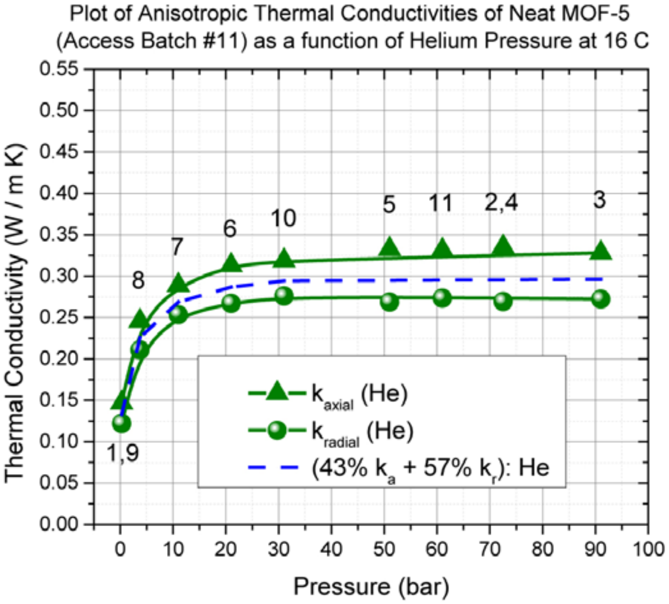

FIGURE 2. Anisotropic thermal conductivities of neat MOF-5 engineered compacts (diameter = 5 cm, height = 1.5 cm, ρ = 0.4 g/mL) as a function of pressure (absolute) with helium at 16°C *(all samples were treated in a UHP N_2 purged oven at 160°C for a minimum of two days, followed by vacuum treatment for 12 hours; average standard deviation for isotropic and anisotropic measurements was ±0.0052 W/m K [helium, 137 measurements])*

conductivities that equal the overall isotropic measurements. In other words, 57% of the isotropic measurement can be attributed to the radial contribution and 43% of the isotropic measurement can be attributed to the axial contribution. The overall trend of the anisotropic measurements agrees well with the isotropic measurements.

Shown in Figure 3 are the measured anisotropic thermal conductivities of neat MOF-5 engineered compacts as a function of pressure (absolute) with hydrogen at 16°C. All measurements were performed at 16°C. The samples are the same as those used for the isotropic measurements. The dashed line in Figure 3 is the weighted contributions of the radial and axial thermal conductivities that equal the overall isotropic measurements. In other words, 58% of the isotropic measurement can be attributed to the radial contribution and 42% of the isotropic measurement can be attributed to the axial contribution. The anisotropic measurements quantify the axial and radial contributions of the thermal conductivity. Similar to the anisotropic measurements performed with helium, the radial thermal conductivity is less than the axial thermal conductivity. However, the axial and radial thermal conductivities do not follow the general asymptotic behavior observed in Figures 1 and 2. The axial thermal conductivity continues to increase beyond 30 bar and may begin to asymptote around 70–90 bar (~0.45 W/m K). The radial contribution is non-monotonic, exhibiting a maximum around 10–20 bar (0.28 W/m K). The radial contribution appears to asymptote around 70 bar (0.25 W/m K). The cause of this behavior is unknown, but we hypothesize that we are not correctly accounting for all the added hydrogen contributions associated with the hydrogen–MOF-5 composites. For example, the overall volumetric heat capacity of the hydrogen–MOF-5 composite is used to determine the radial and axial thermal conductivities. In turn, the volumetric heat capacity is dependent on the gas-phase hydrogen density, hydrogen heat capacity (which is a function of hydrogen ortho and para states, pressure and temperature) and the MOF-5 heat capacity and density. In short, there are a number of subtle contributions that need to be accounted for in order to obtain reliable thermal conductivity measurements—these contributions will be highlighted in a forthcoming publication.

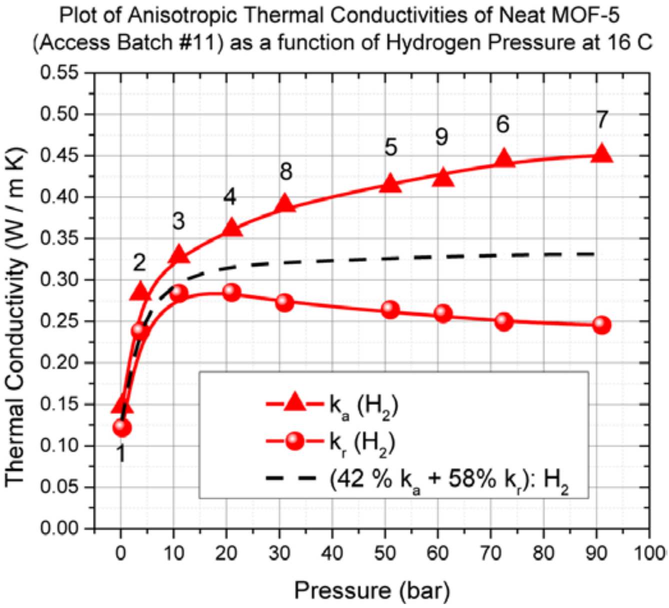

FIGURE 3. Anisotropic thermal conductivities of neat MOF-5 engineered compacts (diameter = 5 cm, height = 1.5 cm, ρ = 0.4 g/mL) as a function of pressure (absolute) with hydrogen at 16°C *(all samples were treated in a UHP N_2 purged oven at 160°C for a minimum of two days, followed by vacuum treatment for 12 hours; average standard deviation for isotropic and anisotropic measurements was ±0.0033 W/m K [hydrogen, 104 measurements])*

CONCLUSIONS AND FUTURE DIRECTIONS

- Designed, built, and tested high-pressure (<100 bar), low-temperature (>-196°C) thermal conductivity cell
- Measured apparent thermal conductivities of neat MOF-5 samples exposed to hydrogen and helium pressures up to 90 bar at 16°C
- Finish thermal conductivity measurements at elevated hydrogen and helium pressures (<100 bar) at liquid nitrogen temperatures (-196°C)